THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INCREASED YIELDS IN ALKALINE PULPING. I. A STUDY OF THE PEELING REACTION AT THE CONDITIONS OF KRAFT PULPING

Project 2942

Report Two

A Progress Report

to

MEMBERS OF GROUP PROJECT 2942

July 10, 1971

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INCREASED YIELDS IN ALKALINE PULPING. I. A STUDY OF THE PEELING REACTION AT THE CONDITIONS OF KRAFT PULPING

SUMMARY

Kinetic data have been obtained in glass reaction tubes for the reaction of cellobiose with 2N sodium hydroxide at 30, 45, and 60°C. Good first-order plots were obtained for the disappearance of disaccharides in the system. Extrapolation of the half-lives for these three temperatures, obtained from the first-order plots, shows a half-life of less than one second at 120°C. This is a much lower value than was predicted. Reactions in the pulping region (150-170°C.) may have to be studied with lower concentrations of alkali to obtain good kinetics, as we are approaching the limits of our flow reactor (0.1 sec. half-life).

A flow reactor has been constructed for operation at 60-90° and is now being used for kinetic studies. Glass syringes drive the several solutions through heating coils and then into a reaction coil for a given period of time. Flow characteristics of liquids through the reactor have been studied, and satisfactory operating conditions established.

A pressurized flow reactor is now being assembled. The driving syringes are contained in a pressure chamber; the liquid is pumped out of the pressure chamber into the heating and reaction coils in an oil bath at atmospheric pressure; the reaction solution is quenched and then returned to the pressure chamber again. This use of a closed loop allows pressure to be maintained at the "open" end of the apparatus (for the quenched sample) and no pressure packings will be needed for the syringes.

INTRODUCTION

DISCUSSION OF KINETIC DATA

This project has been advancing along three fronts — kinetic reaction in glass reaction tubes at lower temperatures, construction of a flow reactor to operate at 60 to 90°C., and construction of a pressurized flow reactor designed to operate at temperatures above 100°C. The first two have been completed and the flow reactor is being used to study kinetic reactions at 60 to 90°C. The pressure chamber for the pressurized reactor has been constructed and the assembly of the reactor is underway.

Three kinetic runs were made of the peeling reaction of cellobiose in 2N sodium hydroxide at 30, 45, and 60°; these were done in special glass tubes in a water bath for periods ranging from 0 to 960 minutes for the 30° run to 0 to 16 minutes for the 60° run. The reaction solutions were mixed manually and quenched with boric acid, the sugars reduced with sodium borohydride and the resulting alditols acetylated and analyzed by gas chromatography. The resulting analytical data are given in Tables I-III and are shown graphically in Fig. 1-3. Satisfactory first-order kinetic plots were obtained for the three reactions, and are given in Fig. 4-6. The experiment at 60° is as far as one can go with manual operations; a flow reactor is being used for kinetic runs above this temperature.

The acceleration of reaction rates with temperature is greater than had been predicted (1) for this project. It had been suggested that the rates would double for every ten degrees rise in temperature; this would amount to a factor of eight for an increase in thirty degrees. Actually, the increase in rates for this temperature difference is about fifty times.

TABLE I

CELLOBIOSE (5.67×10^{-3} M) IN NaOH (1.956N) AT 30.0 ± 0.1°C.

Time, min.	Disaccharide, M, $\times 10^3$	Monosaccharide, M, $\times 10^3$
0	5.67	0.052[a]
15	5.53	0.077
30	5.37	0.098
60	4.91	0.226
120	4.56	0.523
240	3.31	1.32
480	2.09	2.38
960	0.72	2.44

[a]The origin of the monosaccharide at zero time is uncertain.

TABLE II

CELLOBIOSE (5.56×10^{-3} M) IN NaOH (1.956N) AT 45.0 ± 0.1°C.

Time, min.	Disaccharide, M, $\times 10^3$	Monosaccharide, M, $\times 10^3$
0.0	5.63	0.05[a]
5.0	5.37	0.13
10.0	4.48	0.785
20.0	4.54	0.815
40.0	3.29	1.65
60.0	2.26	2.19
100.0	1.10	2.35
160.0	0.45	1.73
240.0	0.14	0.748
360.0	0.09	0.25
480.0	0.00	0.082
	Duplicate Run	
15.0	4.50	0.53
20.0	4.01	0.716
50.0	2.42	1.96

[a]The origin of the monosaccharide at zero time is uncertain.

TABLE III

CELLOBIOSE (5.60×10^{-3} M) IN NaOH (1.956N) AT 60.0 ± 0.1°C.

Time, min.	Disaccharide, M, $\times 10^3$	Monosaccharide, M, $\times 10^3$
0.0	5.64	0.0
2.0	4.70	0.41
4.0	3.69	1.09
6.0	2.88	1.61
8.0	2.38	2.12
10.0	1.84	2.30
15.0	1.07	2.47

An extrapolation of the reaction rates to higher temperatures has been attempted. This has been done through the half-lives, calculated from the rate constants*. The half-life is the time required for one-half of the original reactant to disappear; these are given in Table IV. In Fig. 7 the half-lives for the three temperatures are given in an Arrhenius plot: the log of the half-life against the reciprocal of the absolute temperature. The three points form a slight curve, rather than a stright line, and extrapolation gives a half-life at 120°C. of about one second. This is a long extrapolation, and kinetic data will be determined first at 75 and 90° with the flow reactor, before experiments are carried out with the pressurized reactor.

*$t_{1/2} = (\ln 2)/k = 0.693/k$.

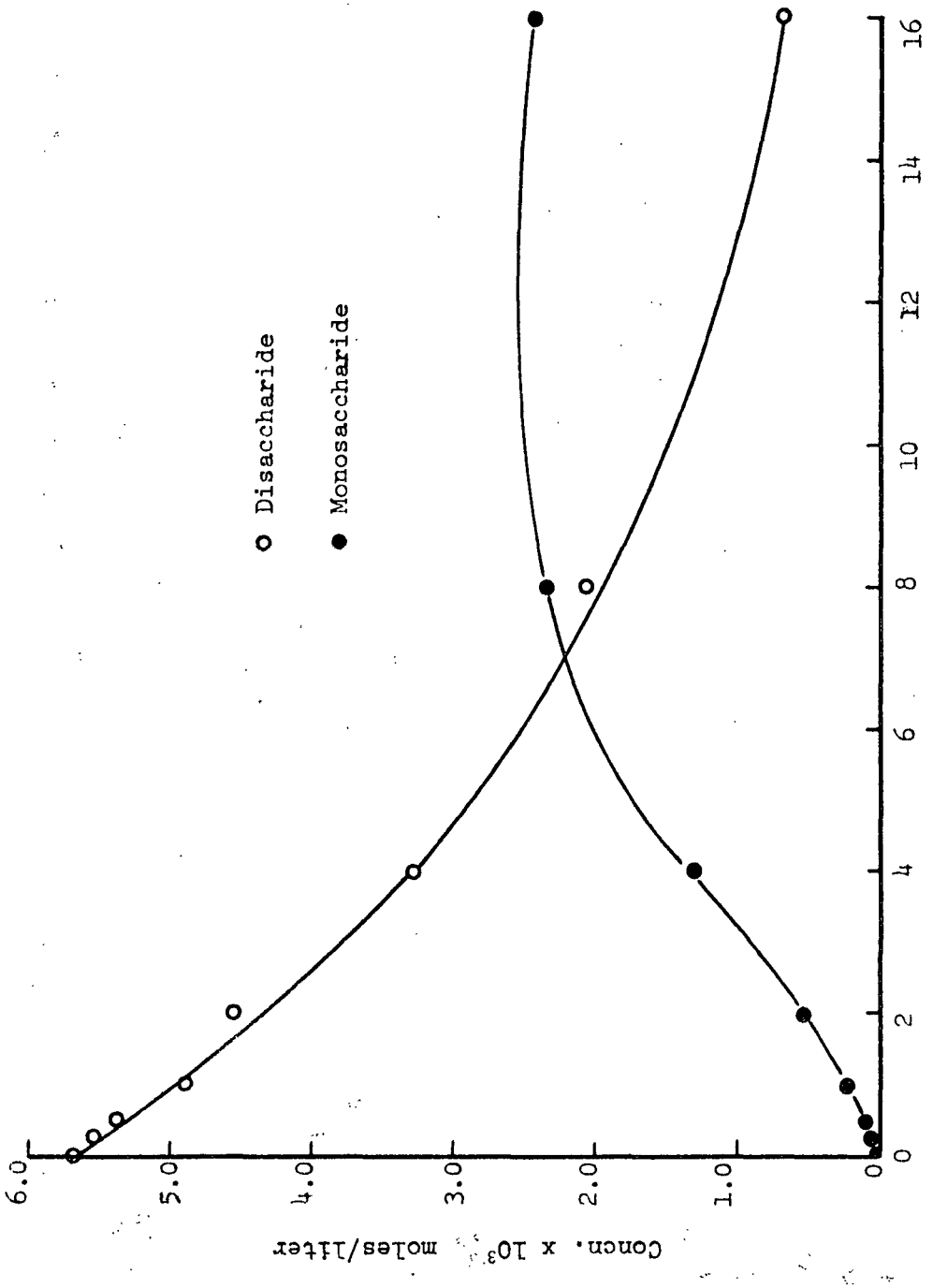


Figure 1. Reaction of Cellobiose with 2N NaOH at 30°C.; Disappearance of Disaccharides and Appearance of Monosaccharides

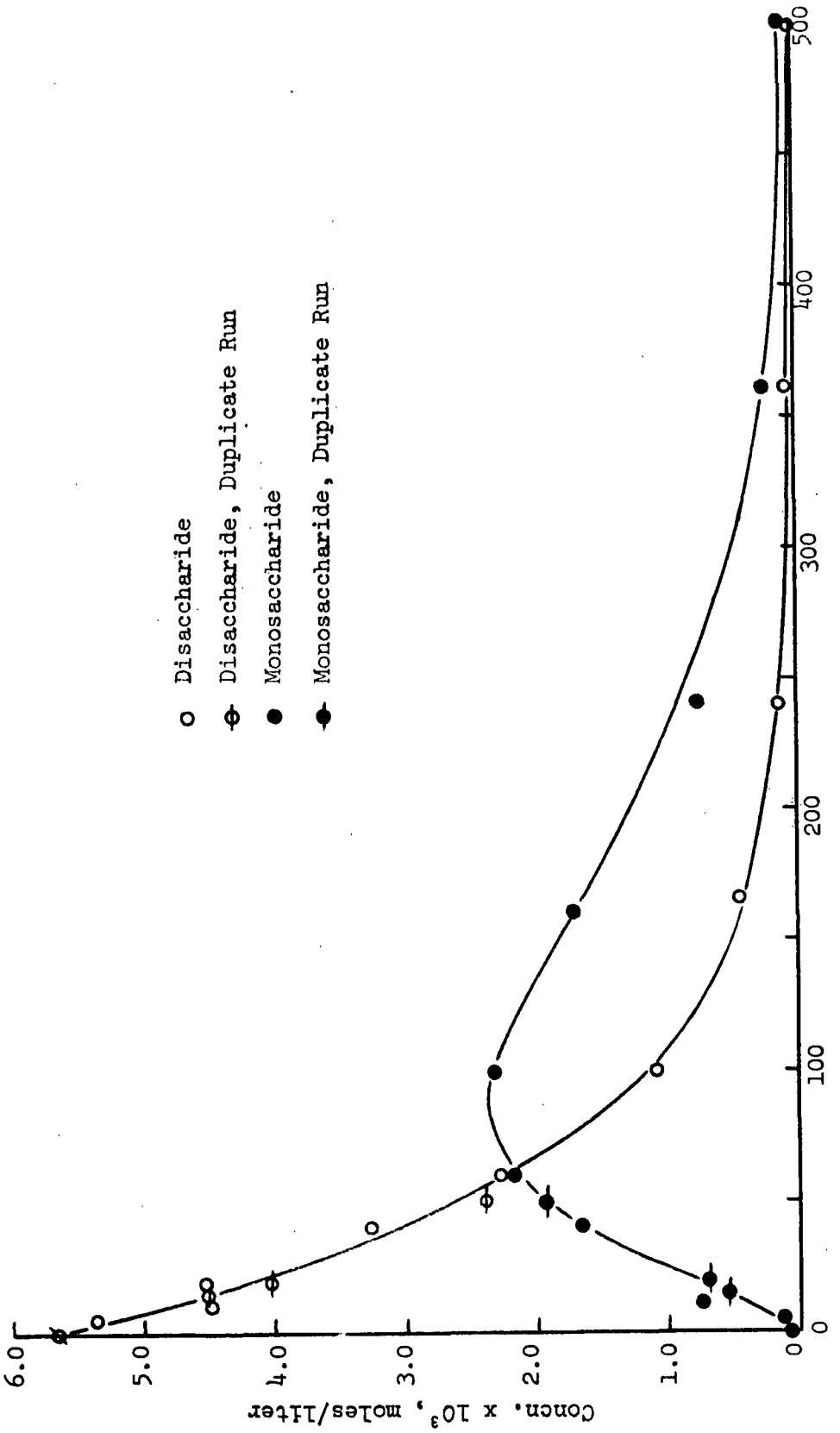


Figure 2. Reaction of Cellobiose with 2N NaOH at 45°C.; Disappearance of Disaccharides and Appearance of Monosaccharides

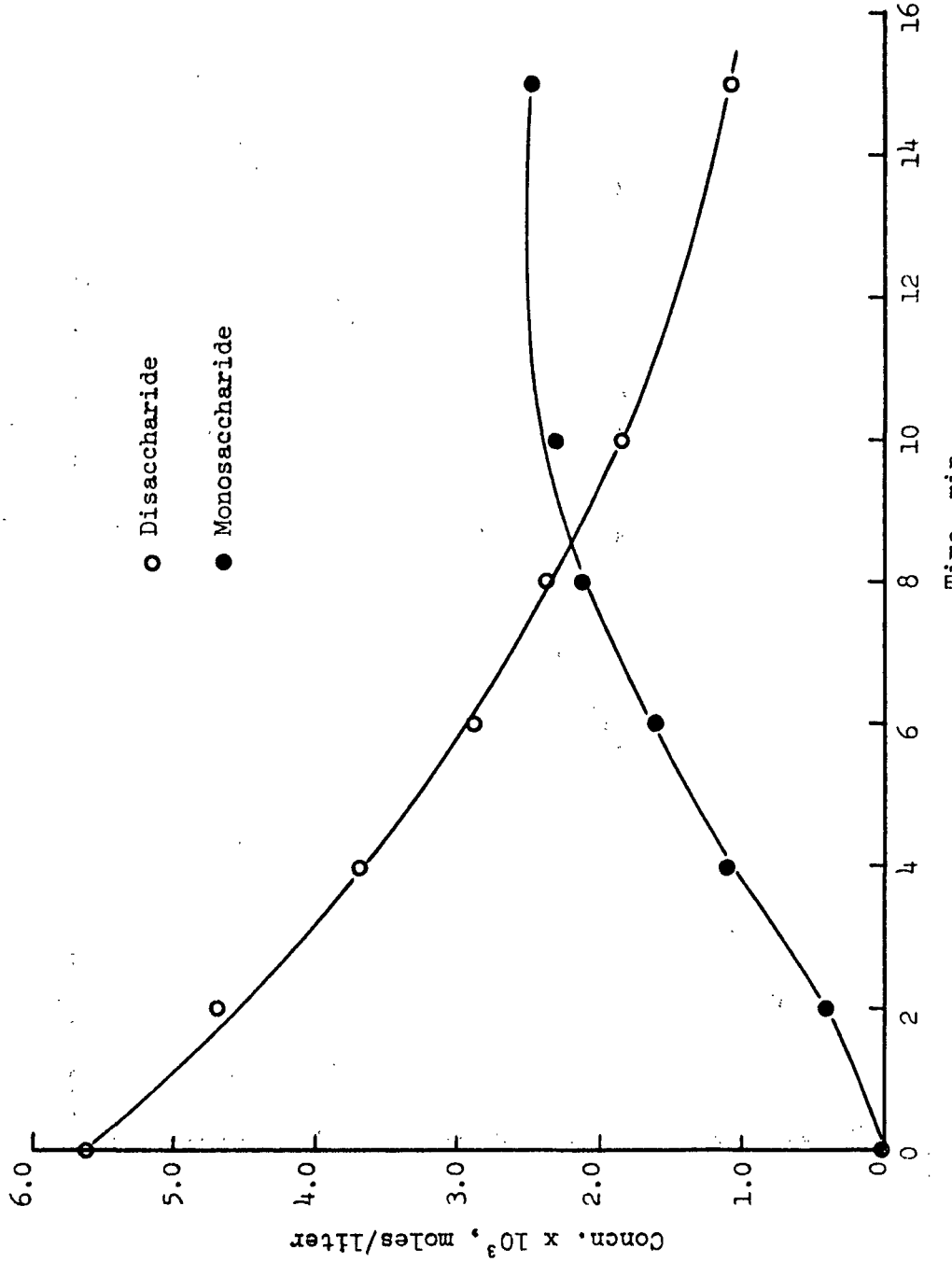


Figure 3. Reaction of Cellobiose with 2N NaOH at 60°C.; Disappearance of Disaccharides and Appearance of Monosaccharides

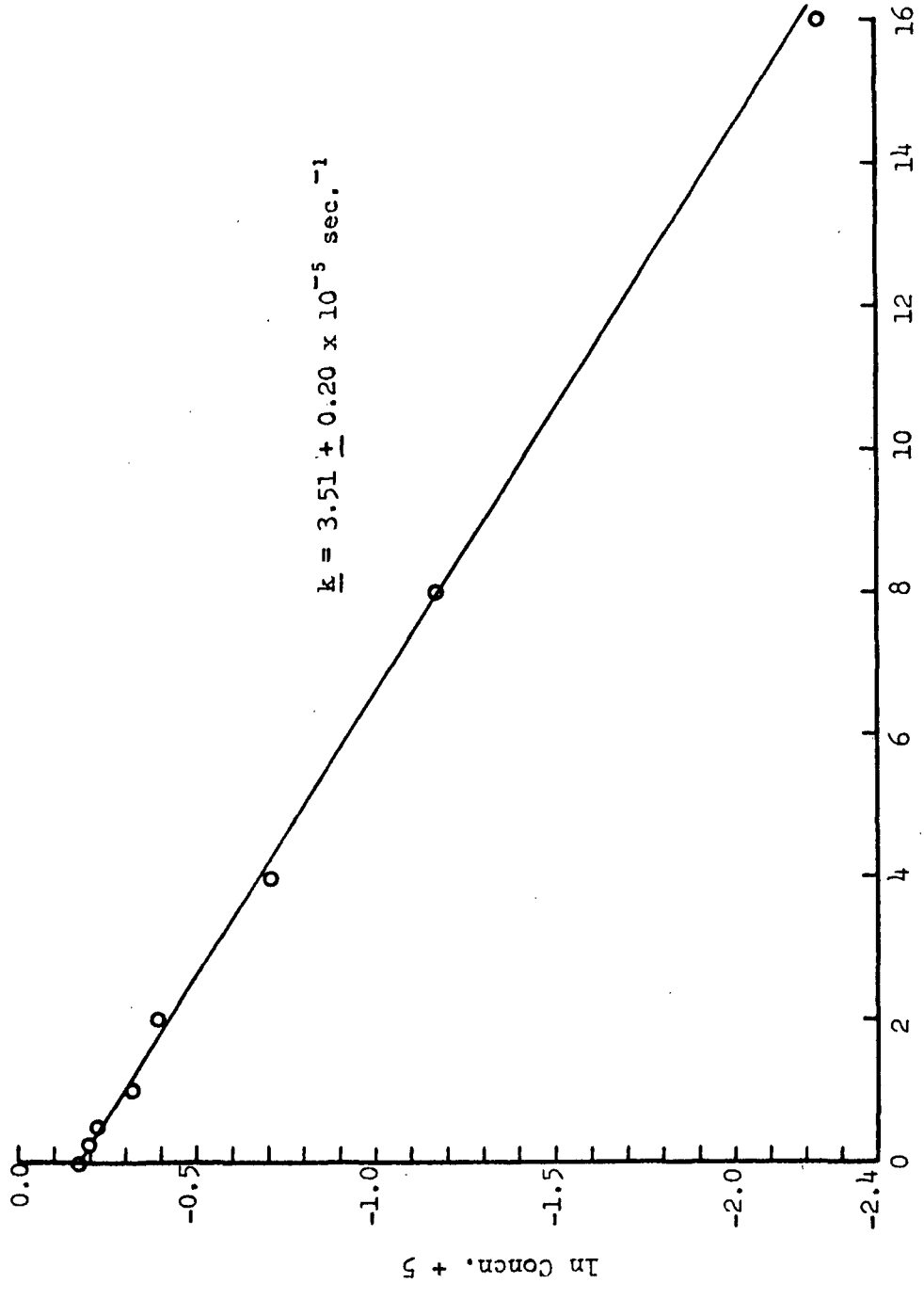


Figure 4. First-Order Kinetic Plot of Disappearance of Disaccharides in the Reaction of Cellobiose with 2N NaOH at 30°C.

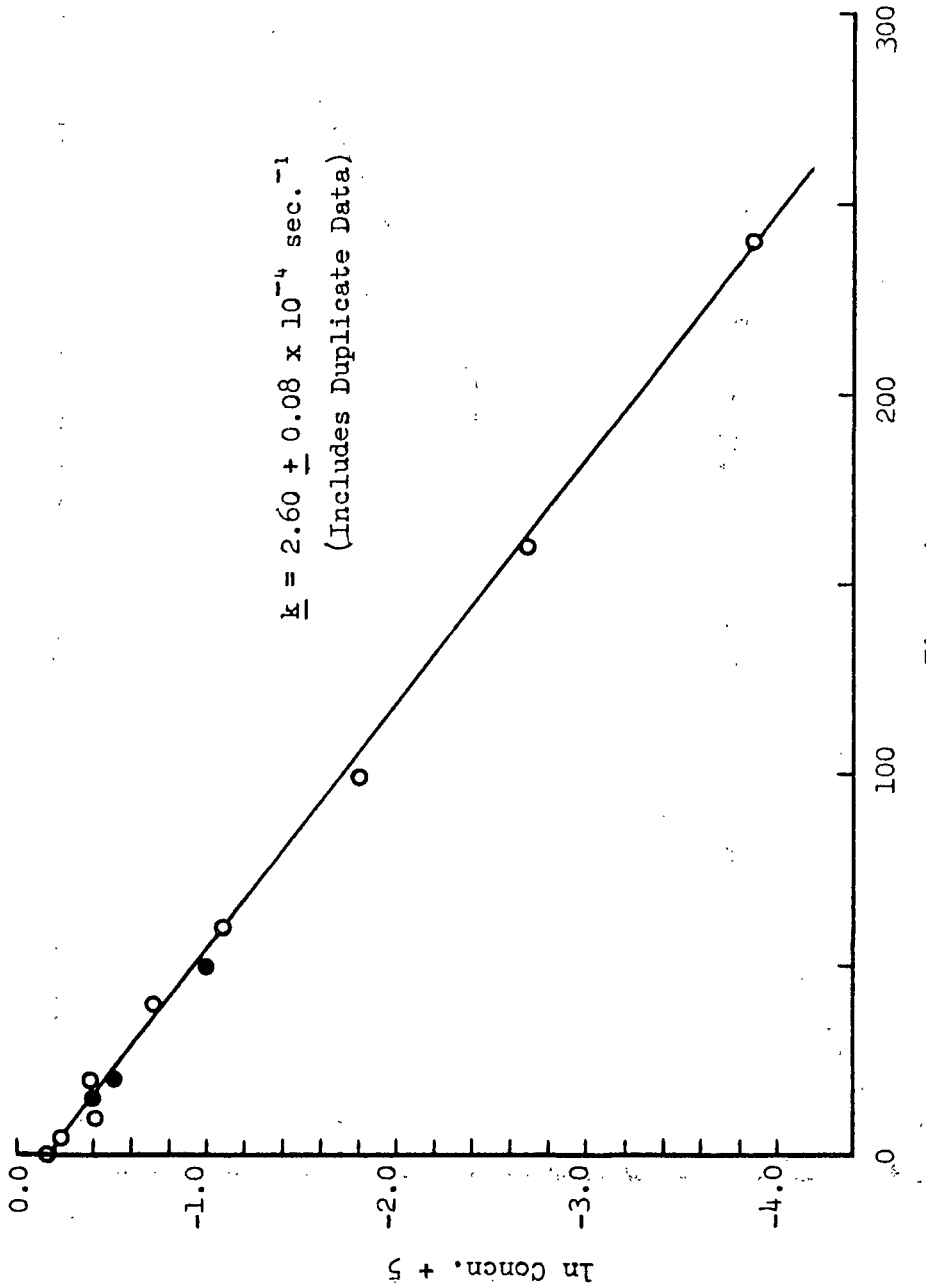


Figure 5. First-Order Kinetic Plot of Disappearance of Disaccharides in the Reaction of Cellobiose with 2N NaOH at 45°C.

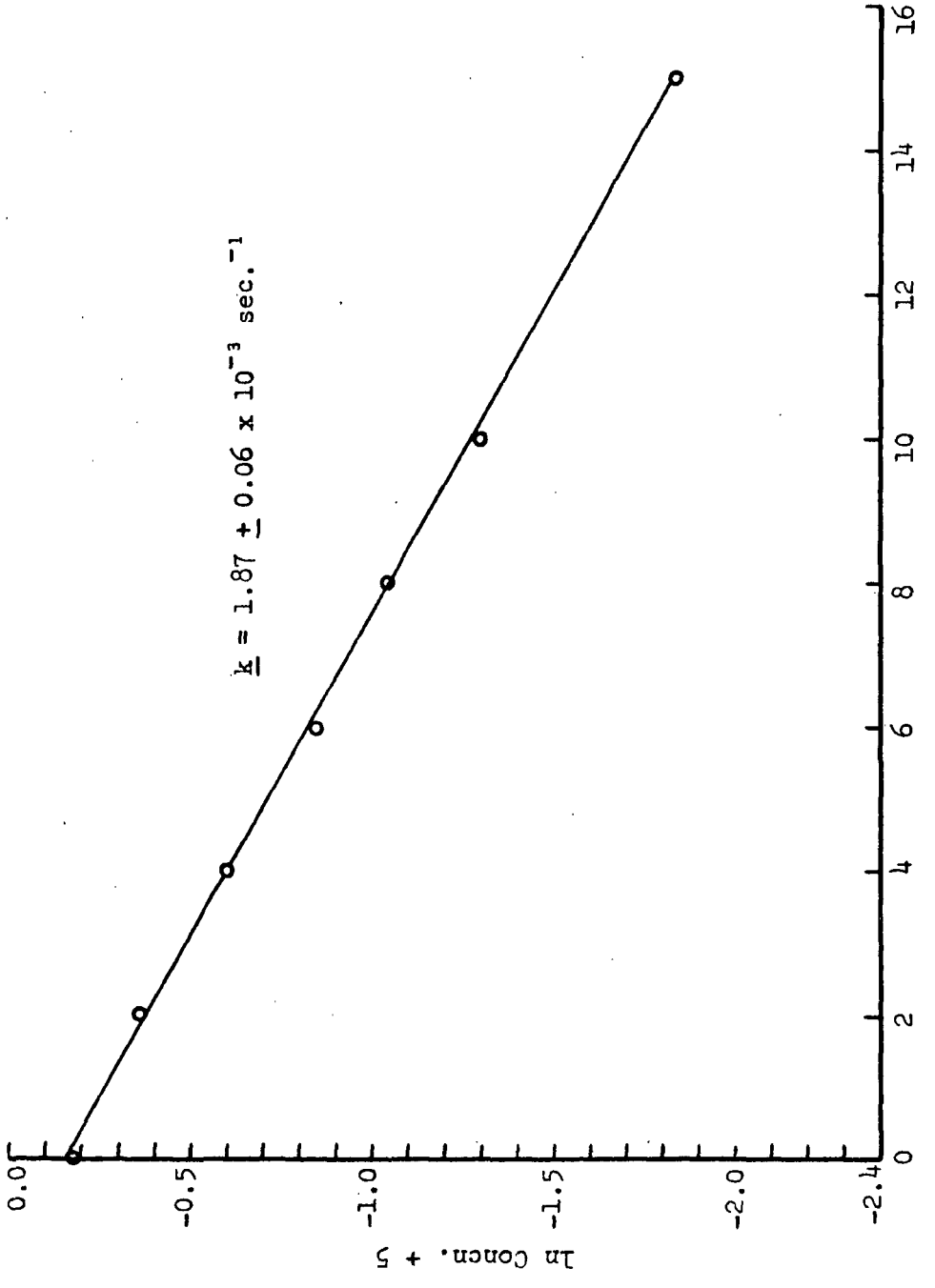


Figure 6. First-Order Kinetic Plot of Disappearance of Disaccharides in the Reaction of Cellobiose with 2N NaOH at 60°C.

TABLE IV

RATE CONSTANT VS. TEMPERATURE

Temp., °C.	k, sec.$^{-1}$	$t_{1/2}$, min.
30.0	3.51×10^{-5}	329
45.0	2.60×10^{-4}	44.4
60.0	1.87×10^{-3}	6.18

Note: From the above data an activation energy of 26.6 kcal. was calculated.

Figure 7 also shows a crude extrapolation of two kinetic points obtained by Lindberg, et al. (2) for the action of less concentrated alkali (0.02N) on cellobiose; such an extrapolation gives a half-life of 5 seconds at 150°C. With the flow reactor limited presumably to the study of fast reactions with half-lives not below 0.1 sec., we may have to use more dilute concentrations of alkali, in the region used by Lindberg, et al. The peeling reaction with 2N sodium hydroxide at 150°C. may be too fast to study, and recourse will then be made to lower concentrations of alkali or to buffered solutions. The disadvantage of dilute alkali is that most of it is consumed in the peeling reaction (formation of saccharinic acid) so an excess cannot be readily maintained.

The effect of sodium hydroxide concentration on the rate of the peeling reaction is shown again in Fig. 8. Here are plotted the data obtained in the present work for 2N sodium hydroxide, that found by Lindberg, et al. (2) for 0.02N sodium hydroxide, and one intermediate point obtained by MacLaurin and Green (3) with 1N sodium hydroxide. The slopes for the first and second set of points are roughly parallel, and the relative half-lives at 60° are 56 and 6 minutes, a ratio of ten for a concentration ratio of 100. This partial

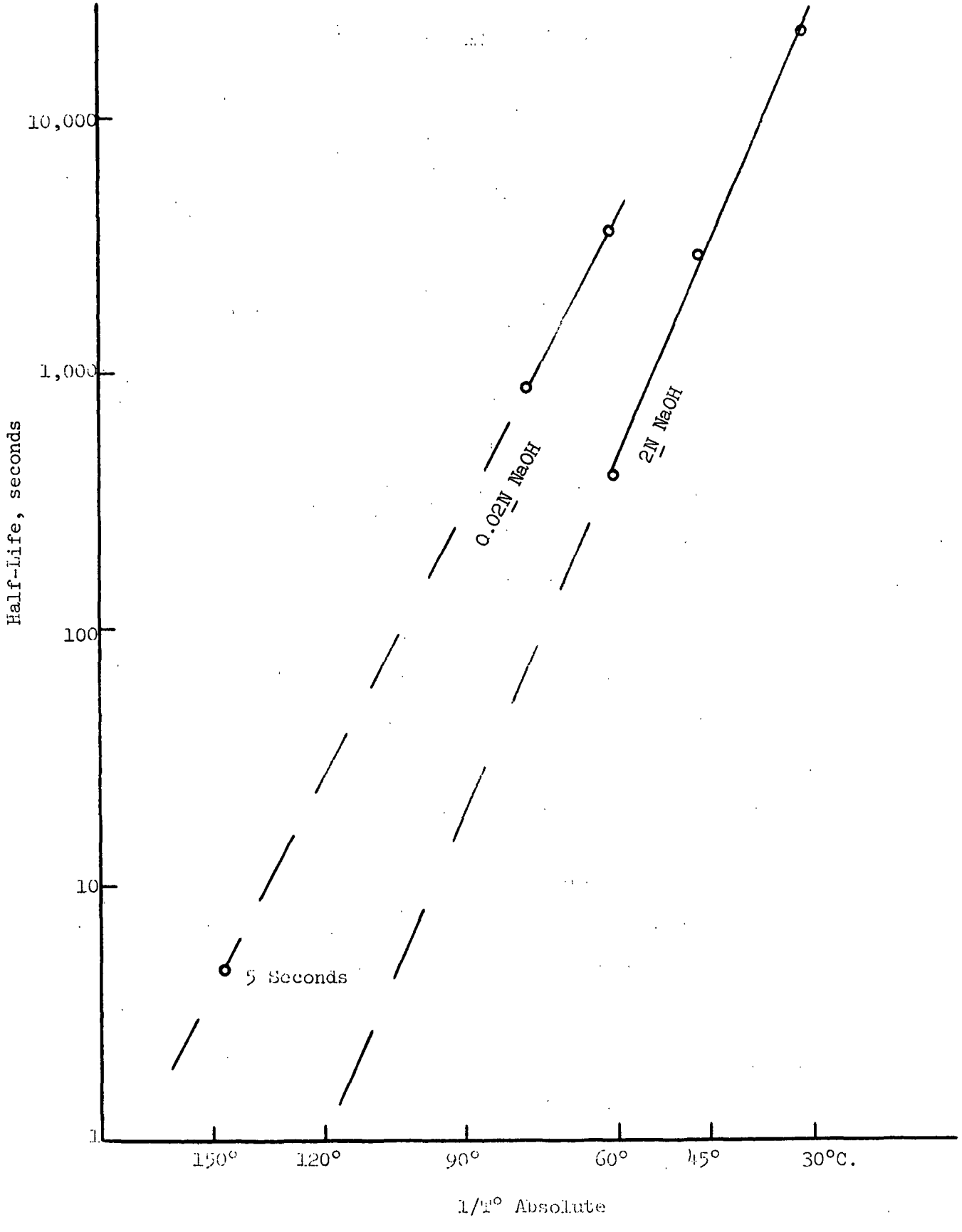


Figure 7. Extrapolation of Kinetic Data to Higher Temperatures

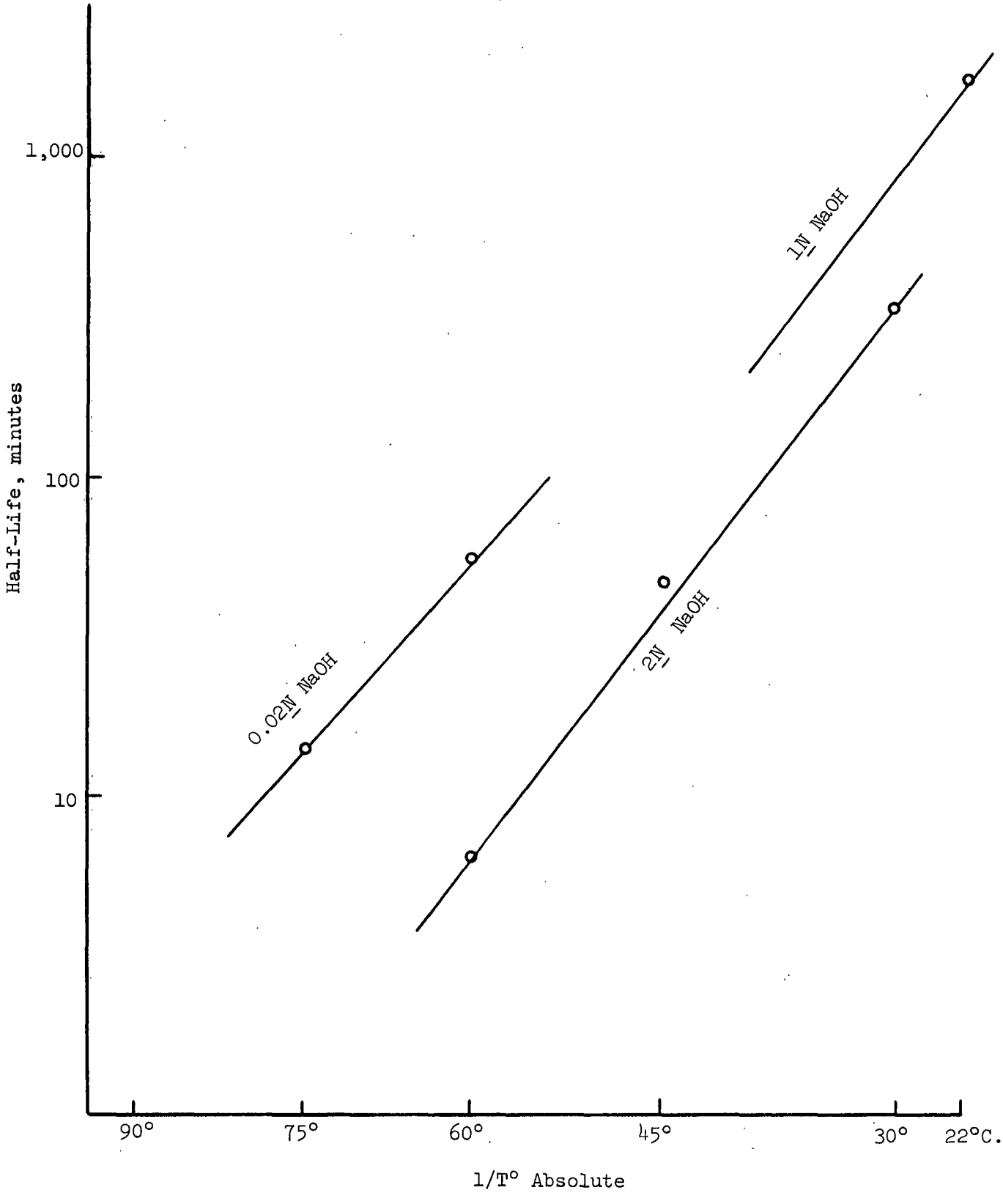


Figure 8. Comparison of Half-Lives of Cellobiose in Sodium Hydroxide of Different Concentrations

dependence of rate on alkali concentration is in contrast to the work of Best (4) who obtained a reaction order of 0.7 for the breaking of glycosidic bonds in alkali ranging from 0.10 to 2.50N concentration. This difference in the effect of alkali concentration for the peeling reaction and glycosidic bond cleavage is interesting and merits further study. Best discussed the effect of activity coefficients and salt effects. To compare peeling at different alkali concentrations, the same ionic strength should be maintained at the lower concentrations that is present for 2N concentration. The same precautions should be observed with the use of buffers, if pH regions below that of 0.02N sodium hydroxide are to be observed.

One would presume that the function of base in the peeling reaction is to remove protons and aid in the formation of a carbanion [probably at C-3 in the intermediate cellobiulose; cf. MacLaurin and Green (3)]. However, the rate of peeling for 2N sodium hydroxide is not 100 times that observed with 0.02N sodium hydroxide. There may be other factors than just the removal of the proton; the ionization of the resulting carbanion and the movement of electrons in a β-elimination (the peeling of the glucosyloxy group) may be affected by the higher ionic strength of the more concentrated alkali. This merits further investigation, either through the use of dilute alkali or of buffered solutions at even lower pH values.

The flow reactor now in operation is being used for kinetic studies at 60 to 90°C. Such reactions will have half-lives in the range of 6 minutes down to 20 seconds and can be easily handled by the driving speed of the syringe pumps. The data obtained will help to confirm or deny the validity of the extrapolations of data from lower temperatures. Normally, Arrhenius plots (log of rate constant plotted vs. the reciprocal of the absolute temp.)

are not used to extrapolate, but only to check for a linear plot in a certain temperature region and therefore establish whether the kinetics for the several temperatures studied represent the same reaction. Linearity of such an Arrhenius plot for kinetic data obtained for reactions from 30 to 120°C. would, for example, show that we are probably dealing with the same reaction throughout this temperature range. At present we do not know very much about the peeling reaction under pulping conditions, for the higher temperatures, for various hydroxide concentrations, for sulfidity, etc. There are many avenues to be explored on the mechanism of the peeling reaction, and they can be discussed at the meeting on this project in July.

KINETIC RUNS AT 30 TO 60° IN GLASS REACTION TUBES

TECHNIQUE OF FILLING REACTION TUBES IN A NITROGEN ATMOSPHERE

The several reaction tubes, empty and with the screw caps loosely fitted, were placed in a vacuum desiccator and evacuated to 30-inches vacuum (Fig. 9). Then nitrogen was slowly bled into the system by careful changing of the three-way stopcock. As the nitrogen entered the evacuated system, the liquid in the bubbler slowly rose; increased nitrogen flow was maintained so that a slow stream of bubbles rose from the bubbler. After 15 minutes, the bubbler speeded up as full nitrogen pressure was obtained in the desiccator.

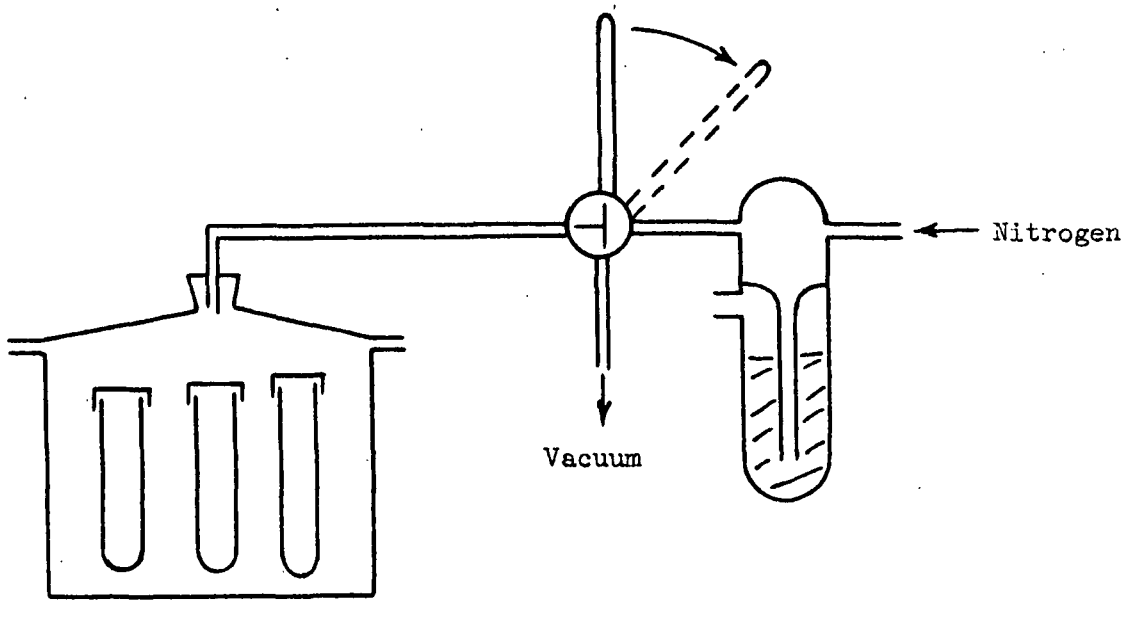


Figure 9. Flushing Reaction Tubes with Nitrogen

This evacuation and flushing was repeated four times and then the closed desiccator placed in a plastic glove bag (see Fig. 10) which was filled twice with nitrogen and pressed flat between fillings to remove any air. The desiccator was opened in the filled bag (the ports shown in Fig. 10 are closed) and the screw caps of the tubes tightened. The bag was opened, the desiccator removed, and the tubes placed in a wooden rack in the bag. Also, a 25-ml. volumetric flask, containing sugar solution, and a 1-liter bottle, containing 2N sodium hydroxide, were placed in the bag. The glove bag was then filled twice with nitrogen.

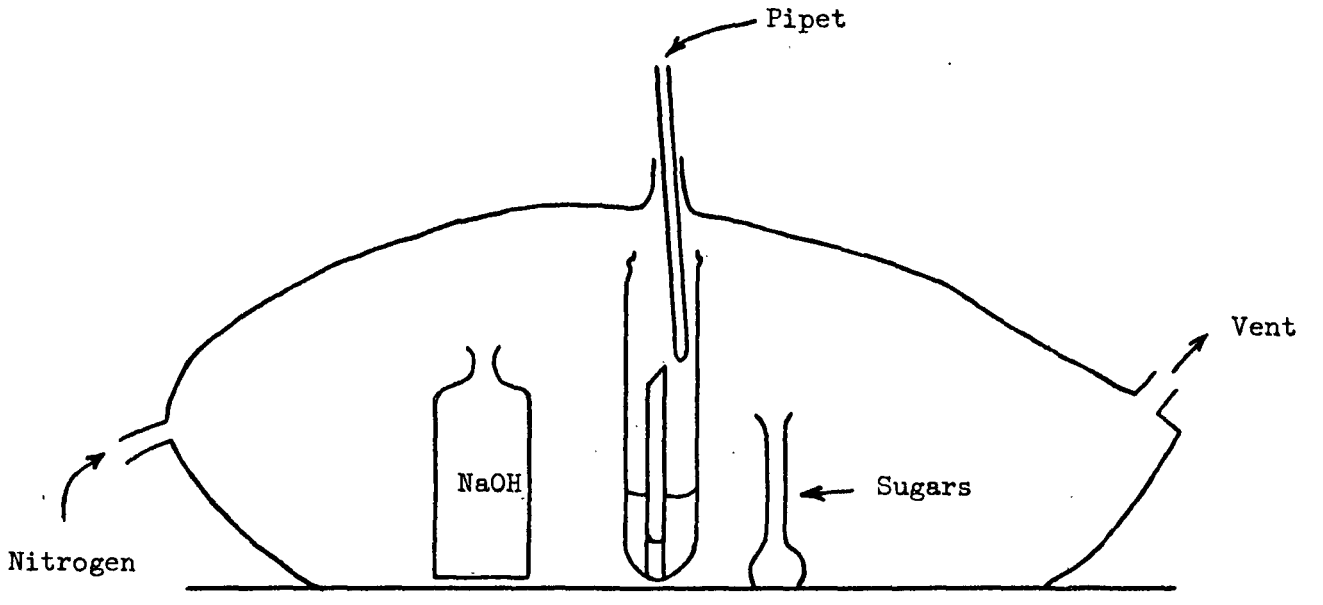


Figure 10. Glove Bag for Filling Tubes

The two ports, sealed with corks, were then opened (Fig. 10). One of these ports was used for introducing a pipet for filling the tubes, and the other port was used for maintaining a slight nitrogen flow through the bag. Each tube

was opened within the bag, and a volumetric pipet (1 ml. or 25 ml.) inserted through the one port from the outside into either the flask or the bottle. It was filled to the mark, and the contents delivered into the inner or outer chamber of the reaction tube. The tube was then closed and the next tube filled in a similar manner. After all the tubes had been filled and the covers tightened, they were removed from the glove bag and placed in the water bath.

All manipulations in the glove bag were done with gloves provided as an integral part of the bag (made of plastic, Model X-37-27, manufactured by Instruments for Research and Industry, Cheltenham, Pennsylvania). They were best done if the bag was only partly filled with nitrogen.

OPERATION OF A KINETIC RUN

The filled tubes, each containing sugar solution in the inner tube and alkali in the outer chamber, were equilibrated in the water bath at the desired temperature for 30 minutes. Most of the tubes were placed in a frame so that they could be inverted and the contents mixed simultaneously. This mixing was done at zero time, during a few seconds and the tubes replaced in the water bath. Then the two zero-time tubes, equilibrated separately in the bath, were each inverted and mixed, and immediately quenched. These zero-time samples had gone through the same heating period (temperature equilibration) as the other samples, but had only a few seconds contact with alkali (that required for mixing and for quenching).

At given times, determined to 0.1 minute with an electric timer (Model C-5D, Reset timer totalizer, Singer-Industrial Timer Corporation, U.S. Highway 287, Parsippany, New Jersey), tubes were removed from the bath and quenched.

QUENCHING PROCEDURE AND REDUCTION WITH SODIUM BOROHYDRIDE

The solution was quickly poured into 130 ml. of 0.5M boric acid in a 400-ml. beaker equipped with a magnetic stirring bar. After 30 seconds stirring (pH 9.8 to 10.0 is obtained immediately), 400 mg. sodium borohydride was added to the beaker from a small plastic dish, stored in a desiccator. The solution was then stirred for a total of 3 minutes to give a clear solution; there was a slight evolution of hydrogen bubbles. The solution was then covered with a watch glass and left overnight at room temperature to complete the reduction.

REMOVAL OF SODIUM IONS AND OF BORIC ACID

Each sample, about 150 ml. solution in a 400-ml. beaker, was treated with 70 ml. IR-120 resin that had been treated with 2N HCl and then washed with distilled water to pH 4.5 to 5.5. The resin was added in portions, with a spoon, as the solution was being stirred magnetically and the pH monitored with a glass electrode.

The initial pH was 9.8 to 10.0. The first addition of resin gave a shift to pH 9 and then slowly dropped to 7. The final drop in pH, to 4.3, was quite slow, during 15 minutes time. In no case was hydrogen evolved with the reduction of pH; apparently, all the borohydride was decomposed during the overnight period. In earlier work, quite a bit of hydrogen was evolved after a 3-hr. period.

The solutions were then filtered through sintered-glass filters into 500-ml. round-bottom flasks and concentrated at 50-60°C. in vacuo to dryness. About 100-ml. wash water was used on the resin, so a total of about 250 ml. filtrate was concentrated.

The residues were then treated with 100 ml. methanol and reconcentrated to dryness (this was done twice) to remove the boric acid present. Initially, there was a large amount of residue, a white bulky powder of boric acid, but after the concentrations with methanol, only a thin sirup remained. There must be no water present or the esterification of the boric acid (to give volatile methyl borate) will not occur.

Each flask was then treated with 50 ml. methanol and the solutions left overnight; this addition of methanol was to prevent fermentation. With nine kinetic samples, it was desirable to get each sample to this stage so that it could be worked up subsequently more leisurely. This removal of water and boric acid was done as rapidly as possible on the day following quenching.

TREATMENT OF RESIDUES WITH MG-3 RESIN

Each of the 9 dried samples was dissolved in 100 ml. water with stirring during 15 minutes. This solution was run through 30 ml. of MB-3 resin in a column (1-inch diameter by 9 inches in length) fitted with a sintered-glass filter and a stopcock. The solution drained through in several minutes, and the resin was washed with 100 ml. water in three portions.

The 200-ml. portions were divided into two equal volumes and one, mixed with 100 ml. ethanol, set aside in the refrigerator as a reserve. The other portion was concentrated in a 500-ml. flask to 10-20 ml. This volume was then transferred to a 100-ml. flask and the larger flask rinsed with a little water. The solutions were concentrated to dryness and reconcentrated with absolute ethanol. The residue was generally a sirup, but the earlier kinetic samples often crystallized.

ACETYLATION OF THE RESIDUES

The flask was dried 15 minutes at 105°C. in an oven. The flask was then allowed to cool to room temperature and treated with 11 ml. of pyridine — acetic anhydride (a mixture of 6 ml. pyridine and 5 anhydride). The residue in the flask generally dissolved within 5 minutes in most cases. In other cases, it was shaken or stirred for several hours. Thus, in the case of the 16-hour samples, there were fine crystals in the flask, so it was stirred magnetically overnight.

The solutions, after 15-20 hours at room temperature, were poured with stirring into 60 ml. of ice and water and stirred 15 minutes. The cloudy solution was then extracted with 3 x 20 ml. of chloroform, and the latter washed as follows:

(1) 60 ml. 1N HCl (heat evolved here),

(2) 60 ml. 0.1N HCl,

(3) 3 x 60 ml. water.

The chloroform solution was then dried briefly over sodium sulfate (30 minutes) and filtered through sintered glass into 100-ml. r.b. flasks (weighed). The latter solutions were then concentrated at 40-45°C. to dryness and weighed to determine the weight of the residues.

GAS CHROMATOGRAPHY OF THE ACETYLATED SUGAR ALCOHOLS

The residues from the chloroform extracts were dissolved in acetone and run on the gas chromatograph (5). Five peaks were observed: the major ones, were for cellobiitol, glucitol and cyclohexyl glucoside acetates. The first two peaks represent the disaccharides and monosaccharides present in the quenched

reaction mixture. Two minor peaks, A_1 and A_4, were noted; the first has the retention time of glucose pentaacetate, but its identity is not definite. The second is unknown. It may be that both are acetates of saccharinic acids, although these should be removed by the MB-3 resin treatment.

KINETIC RUN AT 30°C.

A solution of 1.261 g. cellobiose and 0.973 g. cyclohexyl β-D-glucoside (internal standard) was made up with water to 25.00 ml. Nine reaction tubes were filled under nitrogen with 1 ml. of this solution (= 0.0504 g. cellobiose and 0.0389 g. glucoside) and 25 ml. 2N sodium hydroxide. Seven samples were allowed to react for given periods of time, up to 960 minutes, and the two remaining tubes used as zero-time samples.

KINETIC RUN AT 45°C.

For this run, a solution of 1.2372 g. cellobiose and 0.9660 g. cyclohexyl glucoside was made up to 25 ml. volume with water. The reaction tubes were filled each with 1 ml. of this solution (= 0.0495 g. cellobiose and 0.0386 g. glucoside) and 25 ml. 2N sodium hydroxide under nitrogen as described for the 30°C. run. The several samples were quenched with boric acid and then treated with 400 mg. sodium borohydride. After letting these solutions stand for a period of 6 to 22 hours, a second addition of 400 mg. sodium borohydride was made to insure complete reduction. This was done because of the appearance of a "glucose" peak, A_1, in the 30° run. However, despite the second reduction, the A_1 peak was still present, and so this peak may not be glucose pentaacetate, caused by incomplete reduction.

The several solutions were then treated with IR-120 resin (12 to 20 hours after the second addition of sodium borohydride), and subsequent work up to the acetylation stage and gas chromatography.

KINETIC RUN AT 60°C.

A solution of 1.2455 g. cellobiose and 0.9684 g. cyclohexyl β-D-glucoside was made up to 25 ml. with water. The reaction tubes were filled each with 1 ml. of this solution (= 0.0498 g. cellobiose and 0.0379 g. glucoside) and 25 ml. of 2N sodium hydroxide, equilibrated in the water bath at 60°C. and the reaction carried out in the usual manner. Samples were at time intervals from 2 to 16 minutes, quenched with boric acid and the borohydride reduction, etc., done as for the 30° reaction. No attempt was made to carry out a second borohydride reduction, as the data for the 45° run showed this to be unnecessary.

PREPARATION OF THE INTERNAL STANDARD FOR GAS CHROMATOGRAPHY

Cyclohexyl β-D-glucopyranoside has been selected as the internal standard for the GLC analytical method as (1) it is stable to alkali, and (2) the retention time of the acetate is different from those of the compounds being analyzed. Samples were available at the time, from another project. However, now larger amounts of this glucoside are needed, and the preparation is given below.

Cyclohexanol was purified by refluxing over sodium and then distilling in vacuo. The acetobromoglucose was made in the normal manner described in the literature, starting with 200 g. of glucose α,β-pentaacetate.

The modified Koenigs-Knorr reaction (6) was carried out in a 2-liter 3-necked flask, equipped with ground joints, fluted sides for better stirring, and a teflon blade stirrer. The flask contained the following:

1.5 liters absolute chloroform,

0.5 liter cyclohexanol,

70 grams yellow mercuric oxide,

5.2 grams mercuric bromide,

207 grams Drierite (10-20 mesh), and

140 grams acetobromoglucose.

The reaction mixture was stirred for 8 hours at room temperature and then worked up as follows: (1) The solution, after filtration, was washed with 2 x 2 liters of aqueous 20% KI. (2) The solution was washed with 2 liters of water. (3) The solution was concentrated in vacuo to a sirup, using an oil-seal pump to remove the maximum amount of residual cyclohexanol. (4) This sirup, weighing 216.8 g. and containing much cyclohexanol, crystallized spontaneously. It was dissolved in 400 ml. absolute ethanol and decolorized with activated carbon. Cooling this solution gave 87.5 g. crystalline material. (5) This product was recrystallized from 250 ml. absolute ethanol to give 68.8 g. cyclohexyl β-D-glucoside tetraacetate, m. 120.5-122°C. (literature 120-1°).

The original mother liquor gave an additional 8.3 g., m. 109-111°C.

Deactylation of 51.9 g. tetraacetate with sodium methoxide in methanol and deionization with IR-120 resin gave 31.2 g. sirup that crystallized readily. This was recrystallized twice from ethyl acetate containing 4-5% absolute ethanol. The final product, 16.4 g., m. 134-6°C. (literature 133-7°C.).

A second preparation, starting with 151.2 g. acetobromoglucose, gave 59.6 g. of the glucoside tetraacetate. This will be deacetylated and worked up when needed.

FLOW REACTOR OPERATING AT 60 TO 90°C.

DESCRIPTION OF ASSEMBLY

The flow path of the reactor is shown schematically in Fig. 11. The glass syringes A and S, containing alkali and sugar solution, respectively, are driven by a common motor drive or "syringe pump." The solutions pass through heating coils and then into a mixer M_1, where they form the reaction solution. This solution passes through a "reaction coil" and then into a second mixer M_2, where boric acid is added from a larger syringe B, to quench the reaction. The quenched solution, of lower pH than the reaction solution, is collected in beaker Q.

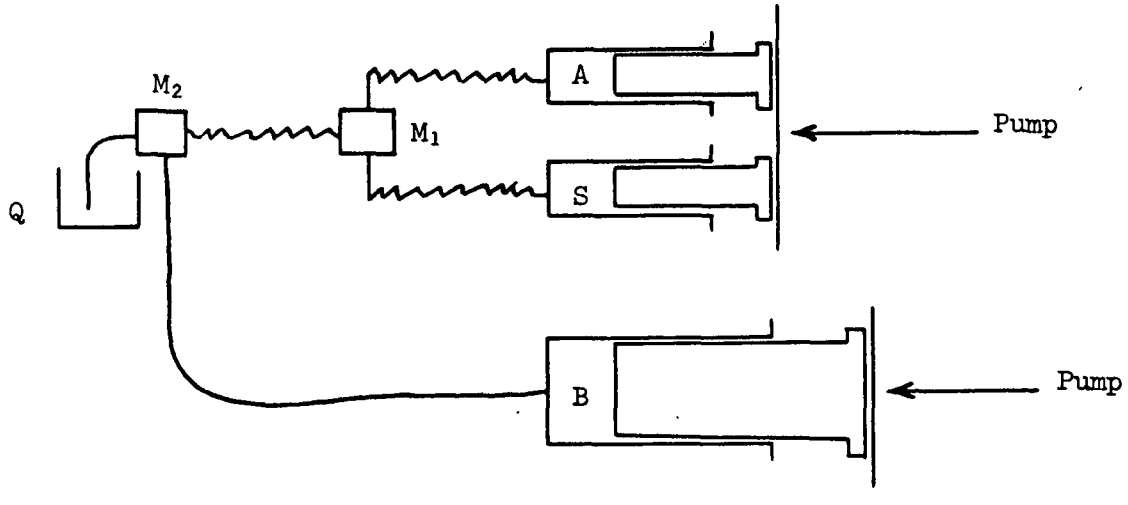


Figure 11. Proposed Flow Reactor (Two Pumps and Quenching System)

The time of reaction depends on the length of the reaction coil and the flow rate in this coil. Such flow reactors, with a quenching feature, have been described in the literature (7). However, heating coils are not normally used, and so the behavior of such coils is discussed in some detail later in this report.

The flow reactor assembly, as used in the laboratory, is shown in Fig. 12. The three glass syringes are mounted on two syringe pumps at two levels on a Lab-Jack. The two 20-ml. syringes are mounted on the lower pump, and the 100-ml. syringe containing boric acid on the upper pump. Each syringe is connected by rubber tubing to a series of three glass stopcocks and a funnel; only one, S_1, is shown in Fig. 12 but the details are shown in Fig. 13 with the various arrangements of the stopcocks.

The heating coils, the reaction coil, and the tubes leading from mixer M_2 are all seamless stainless steel tubing of either 0.125 or 0.085 inch inside diameter, connected by Swagelok fittings. Mixer M_1 is stainless steel and mixer M_2 is Kel-F, mounted in a stainless steel housing. The two heating coils and the long piece of tubing leading to the large syringe are attached by rubber tubing to the respective S_1 stopcocks. Thus, the assembly of 3 coils and two mixers is suspended from the three S_1 stopcocks so that it can be raised and lowered into the oil bath, by operation of the Lab-Jack. The weight of the heating coils is partly taken by a slotted apron fastened to the lower level of the Lab-Jack. The three stopcock-funnel assemblies are secured by clamps to vertical rods on the Lab-Jack. The oil bath is a conventional heating bath, with thermostatic controls and knife heaters.

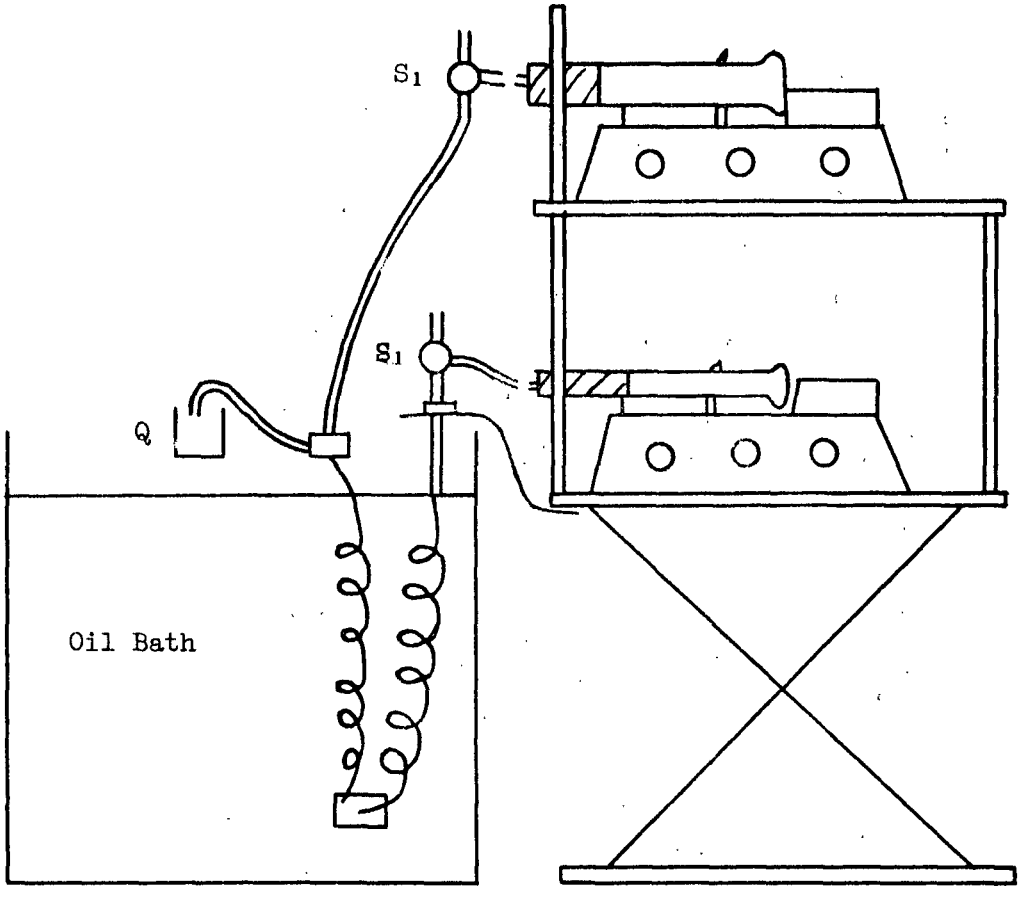


Figure 12. Reactor Assembly, Oil Bath, and Lab Jack (Only One Small Syringe and One Heating Coil are Shown)

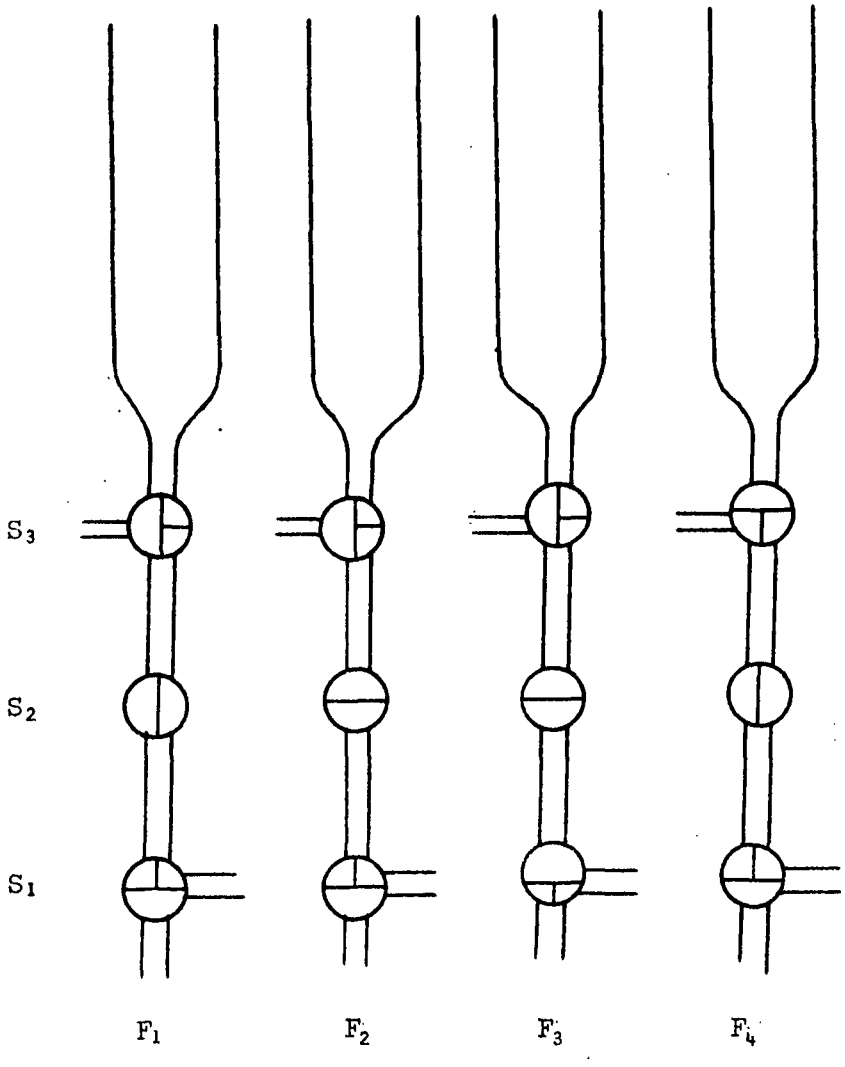


Figure 13. Stopcock Arrangements for Flow Reactor

DETAILS OF THE SYRINGE PUMPS

The type of syringe pump (Model 7122-22, multirate, infusion withdrawal style, Sage Instrument Company, 230 Ferris Avenue, White Plains, New York) used is shown in Fig. 14. It has a clamp for holding syringes up to 100-ml. volume, and a drive carriage operated by a heavy-duty stepper motor which drives the carriage in a series of rapid pulses. There is no inertia and so the pump can be started and stopped instantly. The range of speeds varies from 0.045 to 30 ml./min. for a 20-ml. syringe and from 0.015 to 100 ml./min. for a 100-ml. syringe. When two syringes are driven in tandem, the resulting speed, as in the reaction coil in the present apparatus, is doubled. Thus, a maximum speed of 200 ml./min. can be obtained with two 100-ml. syringes.

DETAILS OF THE STAINLESS STEEL MIXER M_1

This mixer (Fig. 15) is constructed of stainless steel, and has three ports closed by Swagelok fittings; the latter attached to the two heating coils and the reaction coil. It is a block, 1-inch square and about 1.7 inches in length. Two holes, 1/4-inch diameter and 1/2-inch deep, are drilled from opposite ends at P_1 and P_2. They are connected by four 0.05-inch holes (jets) to a mixing chamber, formed by a 1/4-inch diameter hole drilled at right angles, and through the width of the block. This hole is capped at the lower end by a pressure packing with a teflon-coated thermocouple junction, and at the upper end P_3 by a Swagelok fitting.

Thus, liquid entering from the heating coils at the two side ports feed through the jets into the mixing chamber where the temperature is monitored by the thermocouple junction. Ideally, a swirling motion is produced here to provide good mixing, and the solution containing sugar and alkali is fed through

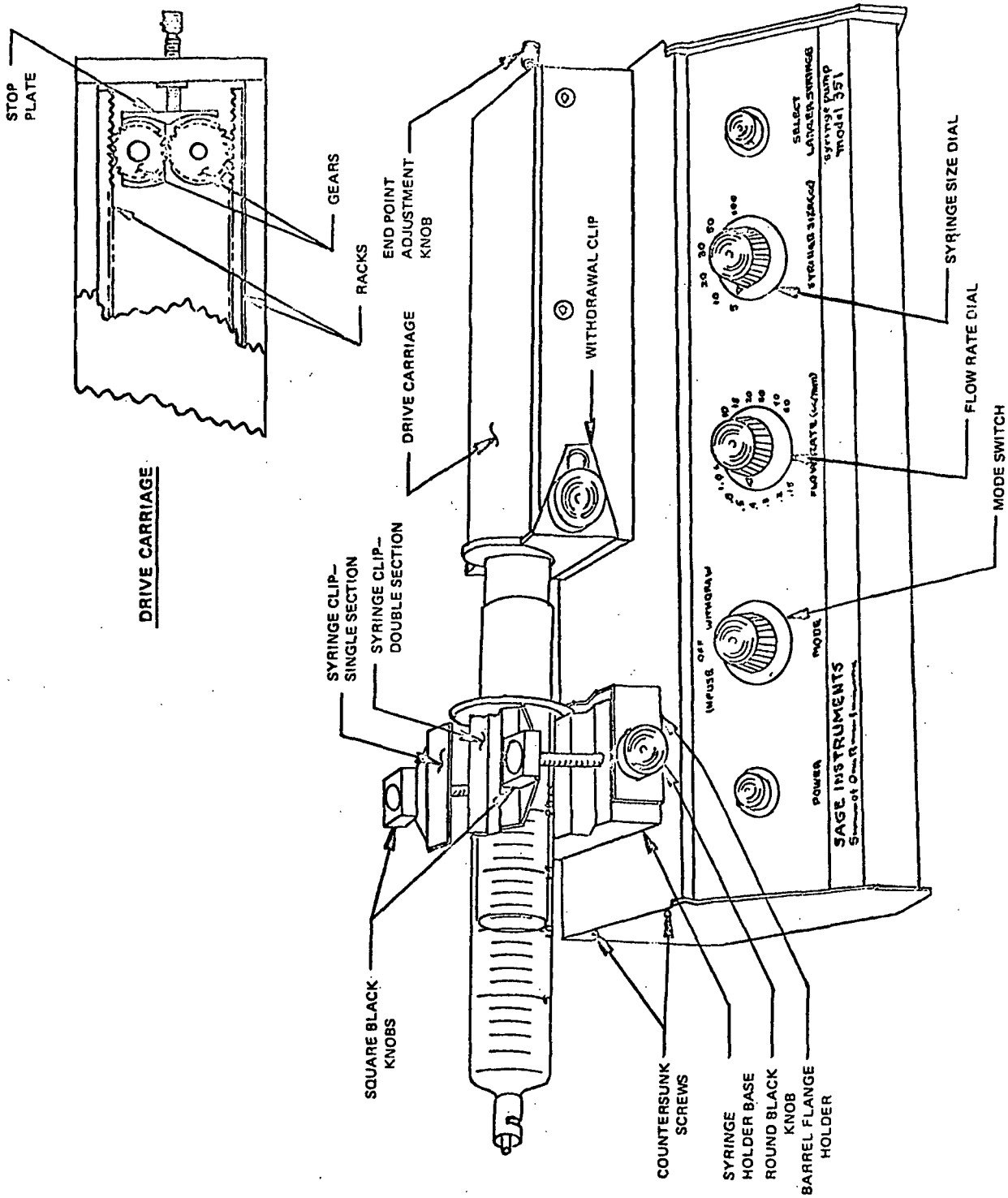


Figure 14. Sage Syringe Pump

P_3 into the reaction coil. Two problems did arise; the jets are not offset very much and there was dead space between the Swagelok fittings and the jets, and also in the mixing chamber. Teflon plugs were machined to fit on P_1 and P_2 to remove dead space in these regions. Also, the dead space in the mixing chamber (about 0.85 ml.) was greatly reduced by being filled with small teflon chips. Before the addition of these chips, mixing of alkali and water was poor; due to the greater density of the alkali, the lower part of the mixing chamber would fill up with alkali and water would "bypass" the chamber. The resultant mixtures were thus initially poor in alkali and richer in water than was expected for a 50:50 mixture.

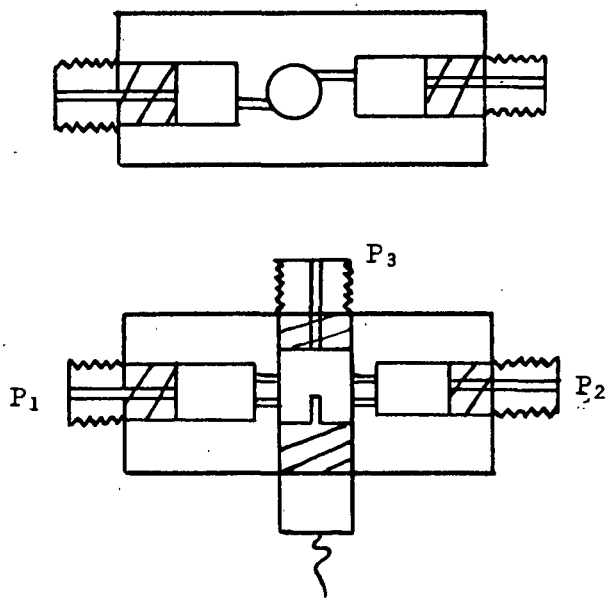


Figure 15. Stainless Jet Mixer, Equipped with Thermocouple

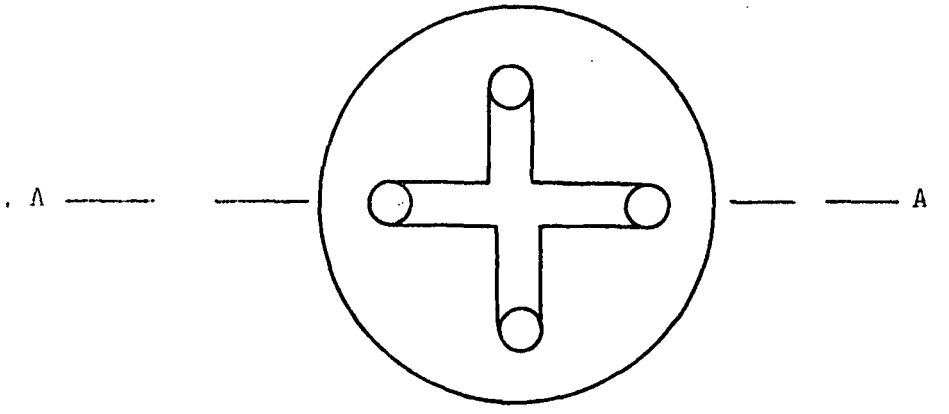
The Gibson jet mixers, described below, are much more efficient in mixing, and have very little dead space and will be used in future work. However, the mixer just described is valuable because of the thermocouple used in measuring thermal equilibration.

DETAILS OF THE GIBSON EIGHT-JET MIXER

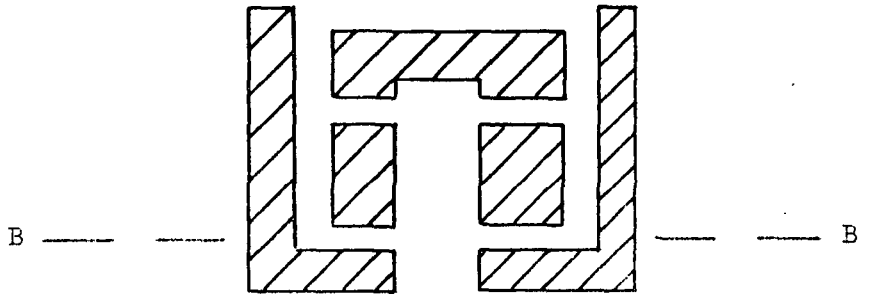
This mixer, made of Kel-F, is shown in Fig. 16. It is very small, only 8-mm. diameter, and with a dead volume of about 0.05 ml. The liquid enters the mixer at the top through four vertical holes, which lead into two sets of jets, mounted to give a swirling action in both clockwise and counterclockwise directions. The horizontal holes forming the eight jets are blind, being drilled from the perimeter and then plugged. This mixer was made by the Durrum Instrument Company of Palo Alto, California, from the design of Gibson and Milnes (8), and has been mounted in a stainless steel housing, fitted with Swagelok fittings, constructed in our shops. Because of the thermal flow of the plastic, this mixer is being used above the surface of the oil bath, in the quenching step. Two such mixers, of stainless steel, have been ordered from the Durrum Company and can be used at higher temperatures. The Kel-F mixer is a standard item carried in stock by the Durrum Company; the stainless mixers are being made as special items.

OPERATION OF THE FLOW REACTOR

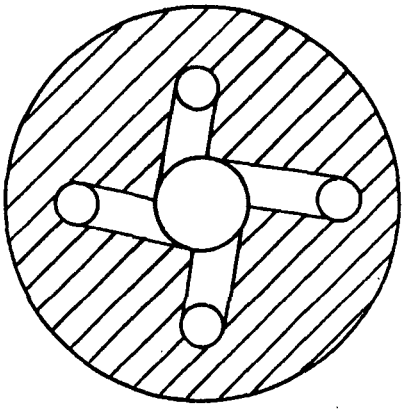
This operation is given as an example of the mixing of alkali and sugar solution, and subsequent quenching with boric acid solution. Later in this report details are given of calibration for flow rates, completeness of mixing, equilibration of temperature in the heating coils, etc.



Top



Section A-A



Section B-B

Figure 16. Gibson Eight-Jet Mixer (Enlarged View — Diameter is 8 mm.)

The three syringes (see Fig. 12) are connected by short pieces of rubber tubing to S_1 of the series of stopcocks, and fastened to the holder base of the syringe pumps by suitable clamps. The two heating coils are also fastened to stopcock S_1 of the lower stage by rubber tubing, and the piece of straight metal tubing leading from the second mixer to the boric acid syringe similarly secured.

The system originally starts with the syringes empty, and the coils and mixers dry (washed with methanol and evacuated). The syringes are first filled with 4N sodium hydroxide, water (as a substitute for an aqueous sugar solution in kinetic runs), and 0.5M boric acid, respectively. This is done by (a) filling the funnel above S_3 (F_4 arrangement of the 3 stopcocks) (Fig. 13) with the given solution, (b) drawing about 10 ml. solution into the given syringe (F_1 arrangement), (c) pushing this solution out of the syringe through the sidearm of stopcock S_3 (F_4 arrangement), and finally filling the syringe (F_1 arrangement) to just beyond the maximum marking (20 to 100 ml., respectively). All of this syringe movement is done manually; the drive carriage of the syringe pump is withdrawn to the far right.

There is generally a small air bubble in the syringe at this stage. The syringe is temporarily removed from the holder base, but is still attached to S_1 by the rubber tubing. It is swung down to a vertical position, so that the tip is upward. The plunger is then moved in slightly so that the air bubble rises out of the tip of the syringe and through the stopcocks into the funnel (F_1 arrangement). The liquid is then pulled back into the syringe and the latter fastened to the holder base again.

At this stage there are three filled syringes, and a series of empty coils and mixers, connected via stopcock S_1 in each case. With the stopcocks in F_4 arrangement, the two motor drives are started at the desired speed (6 ml./min.) until the drive carriages have made contact with the syringe plungers and liquid, driven from the syringes, begins to rise slightly into the funnels. Care must be taken, for the lower syringe pump, that both syringes are in contact with the drive carriage. The pump motors are then stopped, and the stopcocks changed from F_4 to F_2, and then to F_3. Stopcock S_2 must be closed before F_3 arrangement is used, or liquid will drain or siphon into the coils.

The three syringes are now filled and connected directly to the system of coils and mixers. Each stopcock S_1 is the dividing line between the series of solutions and the empty system of coils and mixers. The lower pump is then started and operated at 6 ml./min. for exactly 98 sec. This is the time required for the alkali and water to pass through the two heating coils (5 ml. volume each), the first mixer (about 0.5 ml. volume) and the reaction coil (6 ml. volume). At this predetermined time the mixed solutions should be just making contact with the second mixer.

The upper pump, after 98 sec., is started to supply boric acid at the second mixer; the lower pump is still operating. The liquid emerging from the tube at Q is collected in six 15-ml. samples and the pH of each measured. The data are given in Table V.

In summary: The original alkali has been diluted with an equal volume of water to a concentration of 2N. Five volumes of 0.5M boric acid are needed to quench this 2N sodium hydroxide to a pH of 10. The flow rate in the reaction coil, supplied by two syringes, is twice that of the lower syringe pump, or 12

ml./min. So the flow rate of the upper pump must be ten times that of the lower pump, or 60 ml./min. to give the 5/1 ratio desired at the second mixer.

TABLE V

QUENCHING OF ALKALI IN FLOW REACTOR WITH BORIC ACID

Experiment	Flow Rate of Lower Pump, ml./min.	Flow Rate of Upper Pump, ml./min.	Time to Start Upper Pump, sec.	Volume of Effluent	pH of Effluent
1	6	60	98	15	10.05
				15	10.00
				15	10.05
				15	10.00
				15	10.05
				20	10.10
2	1	10	570	12	4.0
				12	9.0
				12	9.9
				12	10.1
				12	10.2
				12	10.15
				20	10.1
				20	10.1
3	1	10	600	12	9.9
				12	10.0
				12	10.0
				12	10.15
				12	10.1
				12	10.1
				12	10.2
				12	10.1
				15	10.1

Note: The lower pump controls the flow of alkali and water through the coils, and the upper pump the flow of boric acid into the second mixer. The time to start the second pump is the approximate time for the alkaline solution to reach the second mixer.

This is one example of an operation; the reaction coil, of 6-ml. volume and a flow rate of 12 ml./min., would give a reaction time of 30 sec. Other reaction times can be obtained by changing volume and flow rate and this will be discussed later.

CONDITIONS FOR SATISFACTORY OPERATION OF THE REACTOR

The reactor is operated by pumping two solutions through heating coils, through a mixer into a reaction coil and then out of this reaction zone into a quenching system (see Fig. 17). This movement of liquids involves several factors, and they are discussed in more detail following this section. The flow rate is relatively slow and involves laminar flow, which has a parabolic front; the liquid in the center of the tubing moves at a faster rate than that near the walls. At certain stages of the operation a turbulent flow is desired, and at other stages mixing is not desired. The ideal conditions are given below:

(1) The flow of liquid should be at a definite rate, so that the time that the solution stays in the reaction zone can be determined. The Sage pump should be precise at various speeds, and the syringes checked for uniformity of bore, i.e., delivery at various plunger positions.

(2) The pumping of liquid into an empty coil should displace all air (nitrogen) in the coil. This insures a definite volume of liquid in the reaction zone.

(3) The mixer should mix the two solutions very rapidly, and also the two solutions emerging from the syringes and passing through the heating coils should meet simultaneously at the mixer.

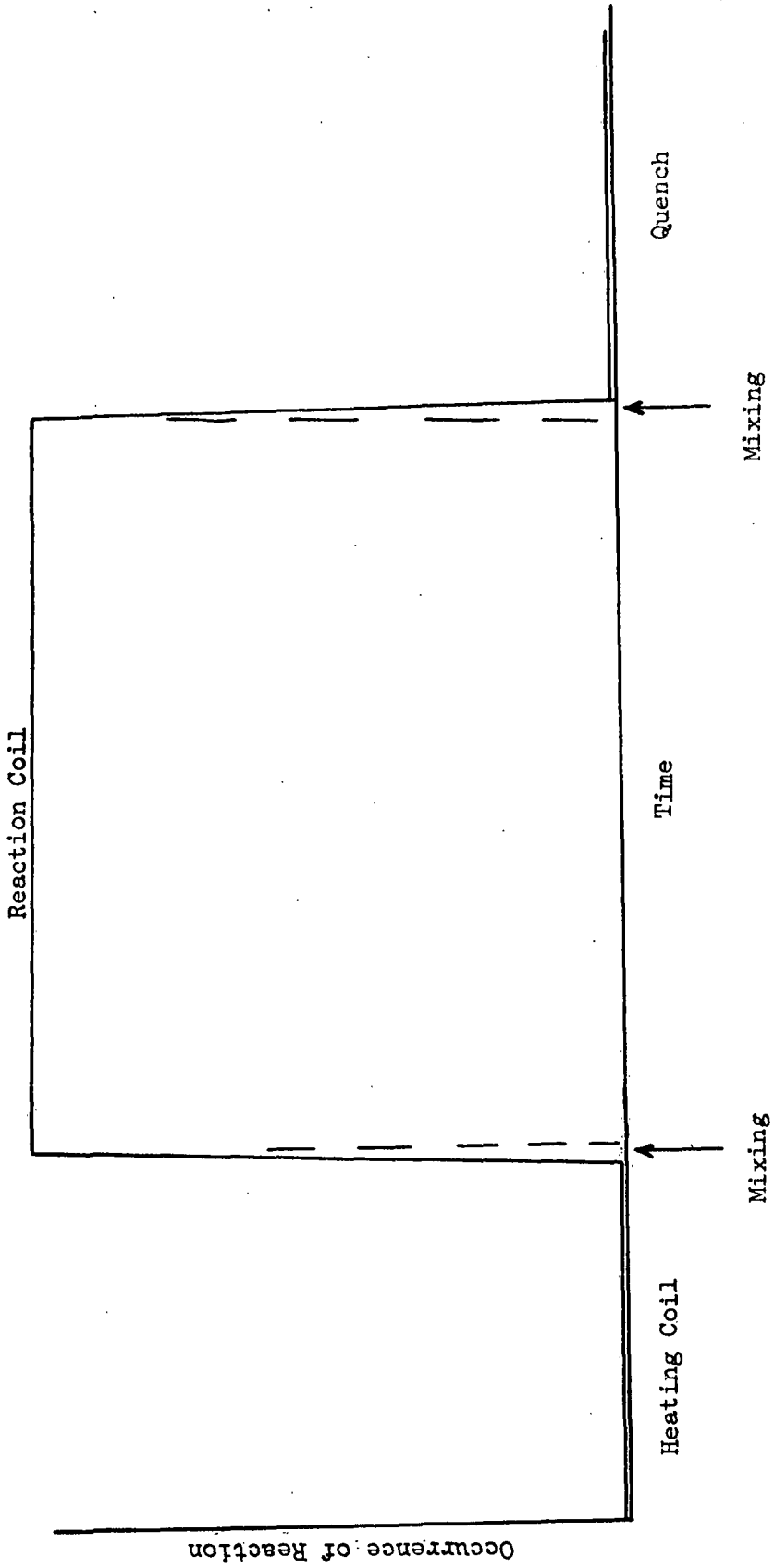


Figure 17. Stages of Reaction in a Flow Reactor

(4) The solutions should be pumped through the heating coils at a limiting rate so that they are at the same temperature as the oil bath by the time they reach the mixer.

(5) The solution in the reaction coil will be displaced by unreacted solution in the heating coils, and that in the heating coils by fresh (cold) solution from the syringes. These "displacing" solutions should not mix with the solution ahead; i.e., "plug" flow should occur.

PRECISION OF FLOW OF WATER FROM SYRINGES

A timing device was connected with the electric circuit of the syringe pump so that the timer and the pump could be started and stopped simultaneously. The electric circuit is shown in Fig. 18. The timer has a one-second dial divided into hundredths of a second, also a 60-sec. dial. A simple glass tube ending in a fine capillary was fastened to the end of the syringe, so that small drops emerged from the syringe. The capillary was directed downward and a weighed beaker placed underneath. Many samples were collected, the beaker being weighed after each time interval, and the weight divided by the time to get the weight of liquid for unit time. As shown in Table VI, the maximum deviation for a 1-milliliter sample was about 0.4%. Also there did not seem to be any great variation within the syringe. Many samples were taken, and the same type of data were obtained from all regions of the syringe barrel.

The syringe pump is calibrated in its speed selections for a certain type of syringe, and in our work, with a teflon plunger we will have to calibrate our given syringes to get a given flow time. Thus, for flow values, on the pump, of 0.3 and 0.6 ml./min. we found values of 0.313 and 0.621 ml./min.

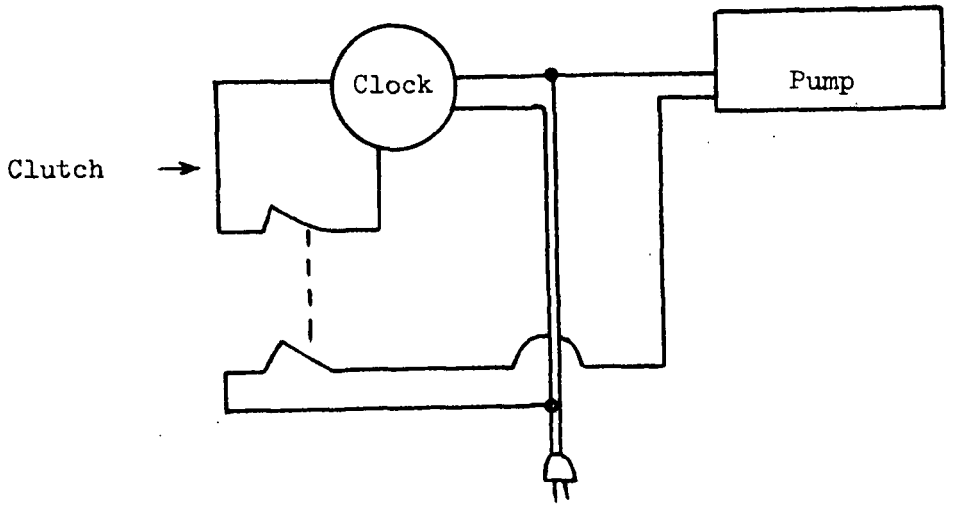


Figure 18. Circuit for Electric Timer

TABLE VI

FLOW RATES OF SYRINGE PUMP AT 1 ML./MIN.

Weight of Beaker, g.	Time of Flow, sec.	Net Weight, g.	Weight/Min.	Deviation per 1000
26.654	0	tare	--	--
27.647	60.16	0.993	0.990	+1
28.635	60.10	0.988	0.986	-3
29.634	60.27	0.999	0.994	+5
30.628	60.25	0.994	0.989	0
31.629	60.29	0.991	0.986	-3
			(0.989 av.)	

A similar type of flow rate testing was done, with two syringes connected to heating coils, mixer and reaction coil. Thus, water was pumped through the reactor system and collected at the exit; the flow rate was twice that set by the pump, as two syringes were involved. The data, given in Table VII, show a precision of 0.5%.

TABLE VII

FLOW RATE OF WATER THROUGH THE REACTOR SYSTEM[a]

Weight of Beaker, g.	Time of Flow, sec.	Net Weight, g.	Weight/Min.	Deviation per 1000
17.739	0	tare	--	--
19.714	60.05	1.975	1.973	+9
21.487	60.20	spilled		--
23.449	60.13	1.962	1.957	-7
25.421	60.18	1.972	1.966	+2
27.385	60.15	1.964	1.959	-5
29.363	60.46	1.978	1.963 (1.964 av.)	-1

[a]Flow rate on dial of pump was 1 ml./min.

A third set of flow rates was taken at a much shorter time interval of 6 sec., to check the starting and stopping inertia of the pump motor. It was expected that this would be a greater factor at these short times, and the data did show a slightly greater deviation. These experiments (Table VIII) were done with a single syringe pumping through a single heating coil, and the 6 sec. times, at 20 ml./min. rate, should give samples of 2 ml. volume or about 2 g. weight.

TABLE VIII

FAST FLOW RATE AT SHORT TIME INTERVALS[a]

Weight of Beaker, g.	Time of Flow, sec.	Net Weight, g.	Weight/Min.	Deviation per 1000
38.836	0	tare	--	--
40.917	6.17	2.081	20.24	+9
42.916	6.00	1.999	19.99	-4
44.958	6.10	2.042	20.08	+1
47.005	6.16	2.045	19.92	-7
			(20.06 av.)	
36.868	0	tare	--	--
38.864	6.03	1.996	19.86	-8
40.878	6.05	2.014	19.97	-2
42.933	6.20	2.055	19.89	-6
45.004	6.18	2.071	20.11	+5
47.061	6.12	2.057	20.17	+8
49.111	6.07	2.050	20.26	+13
51.147	6.12	2.037	19.97	-2
53.188	6.17	2.040	19.84	-8
			(20.01 av.)	

[a]Flow rate of dial of pump was 6 ml./min.

PUMPING LIQUID INTO AN EMPTY COIL

In the previous measurement of flow rates, the flow of liquid was determined in coils already filled with liquid. However, it was desired to measure the volumes of the two heating coils by noting the time required to fill the empty (dried) coils with water. This was done by measuring the exact time required for a drop of water to emerge from the end of the coil. It was found that pumping water downward through the coils gave erratic results (A in Fig. 14) and that pumping upward (B in Fig. 14) gave better results. These data are shown in Table IX. Apparently, some air is trapped in the coils when downward flow is employed.

TABLE IX

PRECISION OF UPWARD AND DOWNWARD FLOW IN COILS

Direction of Flow	Flow Rate, ml./min.	Time to Fill Coil, sec.	Remarks
Downward	2	202.80 205.00 201.45	This is Coil A
Downward	1	392.53 400.35	This is Coil A
Upward	2	210.12 209.23 209.82	This is Coil A
Upward	2	210.52 210.00 210.12	This is Coil B
Upward	2	174.00 172.89 173.25 172.10	This is a 1/8 O.D. coil (0.089 inch I.D.) wound in Style C (see Fig. 14)

The data in the table show the same internal volume for heating coils A and B. The present arrangement of these coils in the flow reactor (see Fig. 12) is for downward flow. Therefore, a modified arrangement (C in Fig. 19) was tried with a 1/8-inch O.D. coil where most of the flow is upward. However, the precision of flow here is not as good as with complete upward flow. The arrangement of the reactor is such that some downward flow will be required, and it is hoped that arrangement C will be an improvement, where flow into empty coils is required.

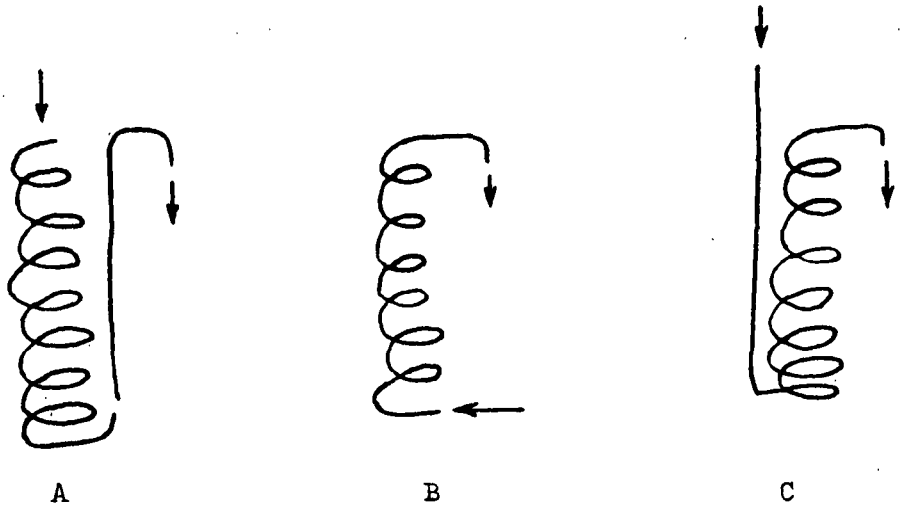


Figure 19. Arrangement of Coils for Up and Down Flow

MIXING OF ALKALI AND WATER IN THE REACTOR

Ideally, if equal volumes of 2N sodium hydroxide and water are fed through the two heating coils into a mixer and then into the reaction coil, the diluted alkali emerging from the reaction coil should be 1N in concentration. This assumption is based on equal flow rates for the two syringes, equal volumes for the two heating coils and efficient mixing in the jet mixer.

In Table X are given data for such mixing, with the stainless mixer M_1. The mixing was done in two ways. The first set of data was obtained by filling the two coils with alkali and water at 1 ml./min., i.e., until liquid just emerged from the exit port P_3 of the mixer. Then the reaction coil was added, the flow changed to 6 ml./min. and the flow resumed. The data show good precision. The second set of data was obtained by using a rate of 6 ml./min. to fill the heating coils and reaction coil continuously, and a similar precision was obtained.

TABLE X

MIXING OF 2N SODIUM HYDROXIDE AND WATER IN STAINLESS MIXER

Time of Flow, sec.	Titer, ml. 0.1N HCl	Titer/10 Sec.	Titer/Average Titer
10.30	18.90	18.35	1.008
10.33	19.10	18.49	1.015
10.20	18.50	18.14	0.996
10.40	18.90	18.17	0.998
10.33	18.60	18.01	0.989
10.10	18.30	18.12	0.995
		(18.21 av.)	
10.39	19.05	18.33	1.008
10.36	18.95	18.29	1.006
10.37	18.80	18.13	0.997
10.45	18.90	18.09	0.995
10.25	18.60	18.15	0.998
10.43	18.90	18.12	0.996
		(18.18 av.)	

Note: In first set of figures, heating coils were filled at 1 ml./min. and mixer and reaction coil at 6 ml./min. In the second set of figures, a flow rate of 6 ml./min. was used throughout.

The coils and mixer have to be dried carefully before such experiments are done. This was done by rinsing the system with water, then acetone or methanol, and drying *in vacuo*. If the coils are not dried carefully (about 15 minutes suction with an aspirator) erratic results are obtained.

Similar results were obtained in the mixing of 4N sodium hydroxide and water. The data are given in Table XI. The increased viscosity of the stronger alkali causes no difficulties. However, in the second set of data in this table, a low value is given; this was apparently caused by the entrainment of air in the coils. This could be noticed by the "spurting" of drops of solution leaving the reaction coil.

TABLE XI

MIXING OF 4N SODIUM HYDROXIDE AND WATER IN STAINLESS MIXER

Time of Flow, sec.	Titer, ml. 0.1N HCl	Titer/10 Sec.	Titer/Average Titer
10.46	36.0	34.42	0.980
10.34	36.5	35.30	1.004
10.41	37.1	35.64	1.015
10.20	35.7	35.00	0.996
10.02	35.3	35.23	1.003
10.35	36.4	35.17	1.001
		(35.13 av.)	
60.37	33.0	(32.80)	low
60.35	35.5	35.29	1.001
60.42	35.7	35.45	1.006
60.45	35.5	35.24	1.000
60.48	35.5	35.22	0.999
60.40	35.3	35.07	0.995
		(35.25 av.)	

Note: First set of data were determined at flow rate of 6 ml./min. and second set at 1 ml./min.

A similar set of mixing tests were carried out with 2N sodium hydroxide and water in the Gibson jet-mixer. This was done at 3 different speeds, with the mixer temporarily connected to the syringes by short pieces (6 inch) of stainless tubing, instead of heating coils. The data, given in Table XII, are of fair precision, but the initial sample in each case is either high or low. It might be best to discard this sample.

TABLE XII

MIXING 2N SODIUM HYDROXIDE AND WATER IN GIBSON MIXER

Time/F Rate of Flow, ml./min.	Time, sec.	Titer, ml. 0.1N HCl	Titer/10 Sec.	Titer/Average Titer
6	10.17	17.6	17.31	0.970
	10.20	18.3	17.94	1.006
	10.31	18.3	17.75	0.995
	10.32	18.6	18.02	1.010
	10.12	18.3	18.08	1.014
	10.43	18.7	17.93	1.005
			(17.84 av.)	
3	20.23	18.2	8.997	0.989
	20.31	18.5	9.109	1.001
	20.23	18.65	9.219	1.013
	19.12	17.0	8.891	0.977
	19.32	18.60	9.154	1.006
	19.29	18.70	9.216	1.013
			(9.098 av.)	
1	60.31	18.80	3.117	1.026
	60.28	18.20	3.019	0.993
	60.32	18.00	2.984	0.982
	60.23	18.40	3.055	1.005
	60.41	18.30	3.029	0.997
	60.35	18.30	3.032	0.998
			(3.039 av.)	

MIXING OF BORIC ACID AND ALKALI; TIMING OF THE QUENCHING REACTION

In Table V, three experiments were given where the quenched effluent had a pH in the region of 10, as desired. The alkaline solution was allowed to flow through the reaction coil for a definite time and then the boric acid flow was started. Ideally, the two solutions should meet simultaneously at the second mixer and quenching will occur rapidly. In Experiments 1 and 3 this mixing was well timed and a pH of 10.05 and 9.9 was obtained with the initial samples of effluent. In Experiment 2 the boric acid reached the mixer first and the initial effluent had a low pH of 4.0.

While the time to start the second pump is determined by separate experiments (time required for solutions from the two small syringes to reach the second mixer), it has some experimental error in it. Thus, as in Experiment 2, the boric acid reached the mixer first. This is not objectionable, but the reverse is, the early arrival of alkaline solution, with a time delay in quenching. Therefore, it might be advisable in kinetic runs to time the flow so that the alkaline sugar solution meets some acid solution at the mixer. The same precaution should be taken in the mixing of sugar solution and alkali at the first mixer; the alkali should arrive at the mixer first, so that the sugar solution is mixed with an excess of alkali at the proper time.

The "leading" of a little alkali solution at the first mixer, or of acid at the second mixer, will cause no harm, since we are analyzing the composition of the sugar solution. Also, there should be no back-flow of solutions at the two mixers, as long as liquid flow is occurring in both ports leading into the given mixer. Air displaced ahead of the solutions will prevent cross-flow.

The "leading" can be done by (a) making the volume of heating coil for the alkali slightly less than that of the heating coil for the sugar solution, and (b) timing the start of the upper pump so that boric acid reaches the mixer first, i.e., as in Experiment 2.

TEMPERATURE EQUILIBRATION OF HEATING COILS

Earlier calculations gave a minimum value of 25 sec. for temperature equilibration of heating coils with a bath temperature of 90°C. and an intake temperature of 20°C.; a fourfold factor was recommended, giving a value of about 2 minutes. The present data given below confirm these calculations.

The reactor system was immersed in the oil bath at 3 given temperatures, with the heating and reaction coils filled with water. Both thermocouple junctions were immersed in the bath, that built into the mixer and the "cold" junction. Since both junctions were at the same temperature, there should ideally be no voltage difference. Actually, a difference of about 0.12 millivolt was found, probably due to a difference in the composition of the two iron-constantan junctions. A plot of temperature vs. difference in voltage is shown in Fig. 20.

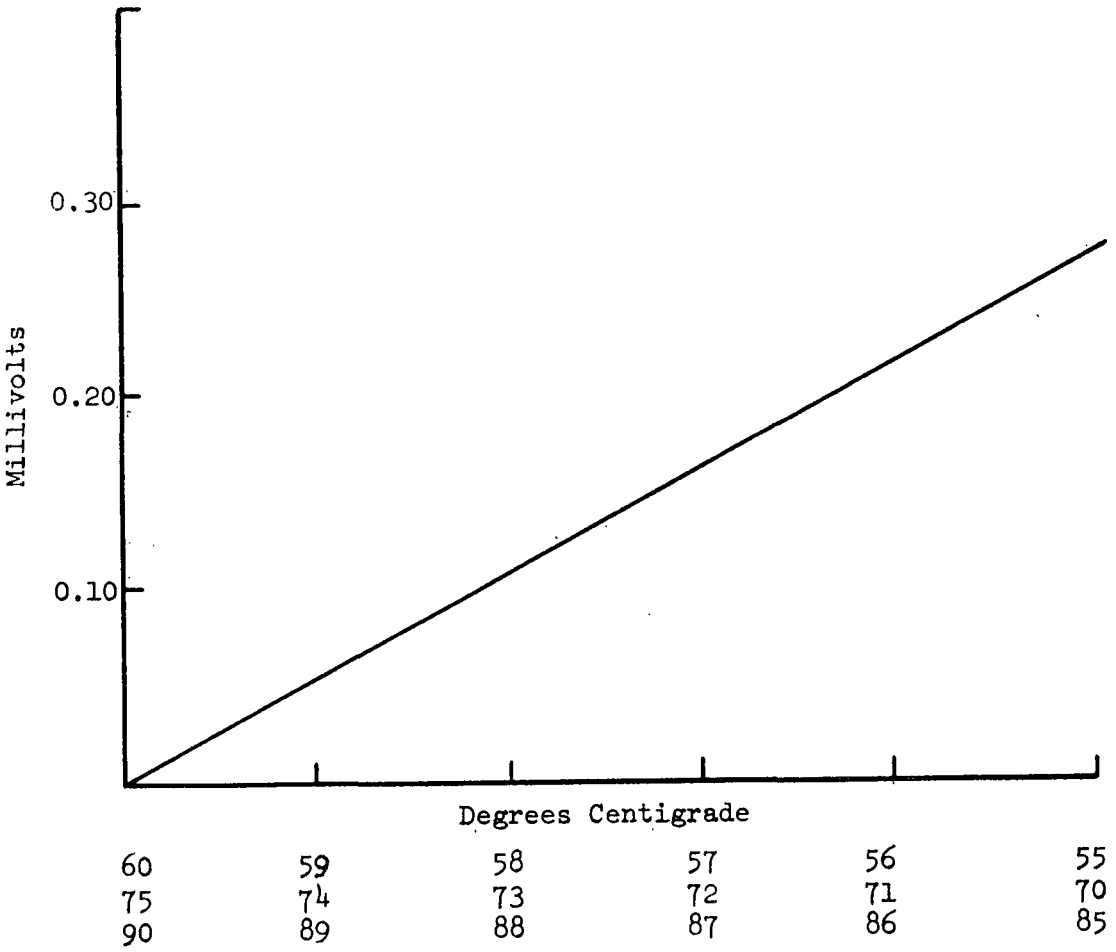


Figure 20. Calibration Chart for Thermocouple

After a constant voltage difference or base line was established, showing that the mixer was at the bath temperature, water was pumped through the heating coils into the mixer at four different rates and at three bath temperatures. As the three plots (Fig. 21-23) show, there were strong temperature drops at the higher flow rates of 15 and 30 ml./min. per syringe. At 4 ml./min. there is no temperature change; for a volume of about 8 ml. for each coil and the 4 ml./min. flow rate, this would mean a dwell time of 2 minutes.

It is interesting that at 90°C. there is more equilibration at 8 ml./min. than at lower temperatures; apparently, it is a matter of a greater temperature difference giving a faster heat flow. However, for higher flow rates the temperature drop is greater, an effect going the other way.

The original data, in millivolts and in temperatures recorded, are given in Table XIII. "Deflection" signifies the initial temperature drop.

PLUG FLOW IN THE HEATING COILS

For the successful operation of the flow reactor, liquid must be "pushed" from the heating coils through the mixer into the reaction coil and then from there into the quenching system. This "pushing" will be done by cold solution from the two syringes containing extra reagent; we are using unreacted solutions to drive reacted solution through the system. In the narrow tubes used it is best, if "plug" flow occurs, that the pushing solution does not mix too much with the solution being pushed. The data obtained showed that, in a single coil, such flow is initially good, a "square" curve being obtained (see Fig. 24); at the end of the flow the curve is not as sharp. Kramers and Westerterp (9) have discussed this, in regard to "residence time distribution in a tubular reactor with longitudinal dispersion"; their S-shaped curve for a real reactor has the same

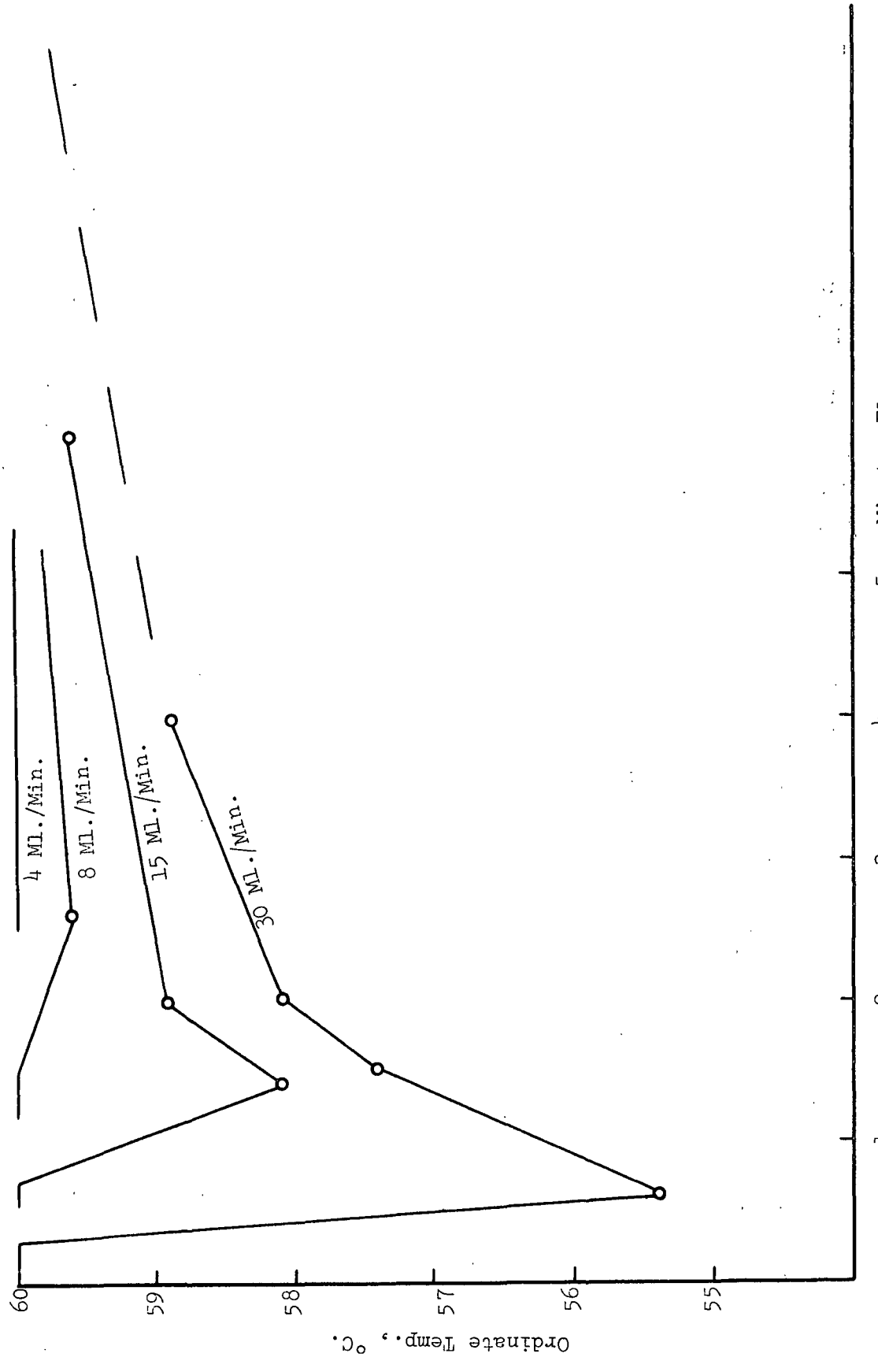


Figure 21. Temperature Equilibration at 60°C.

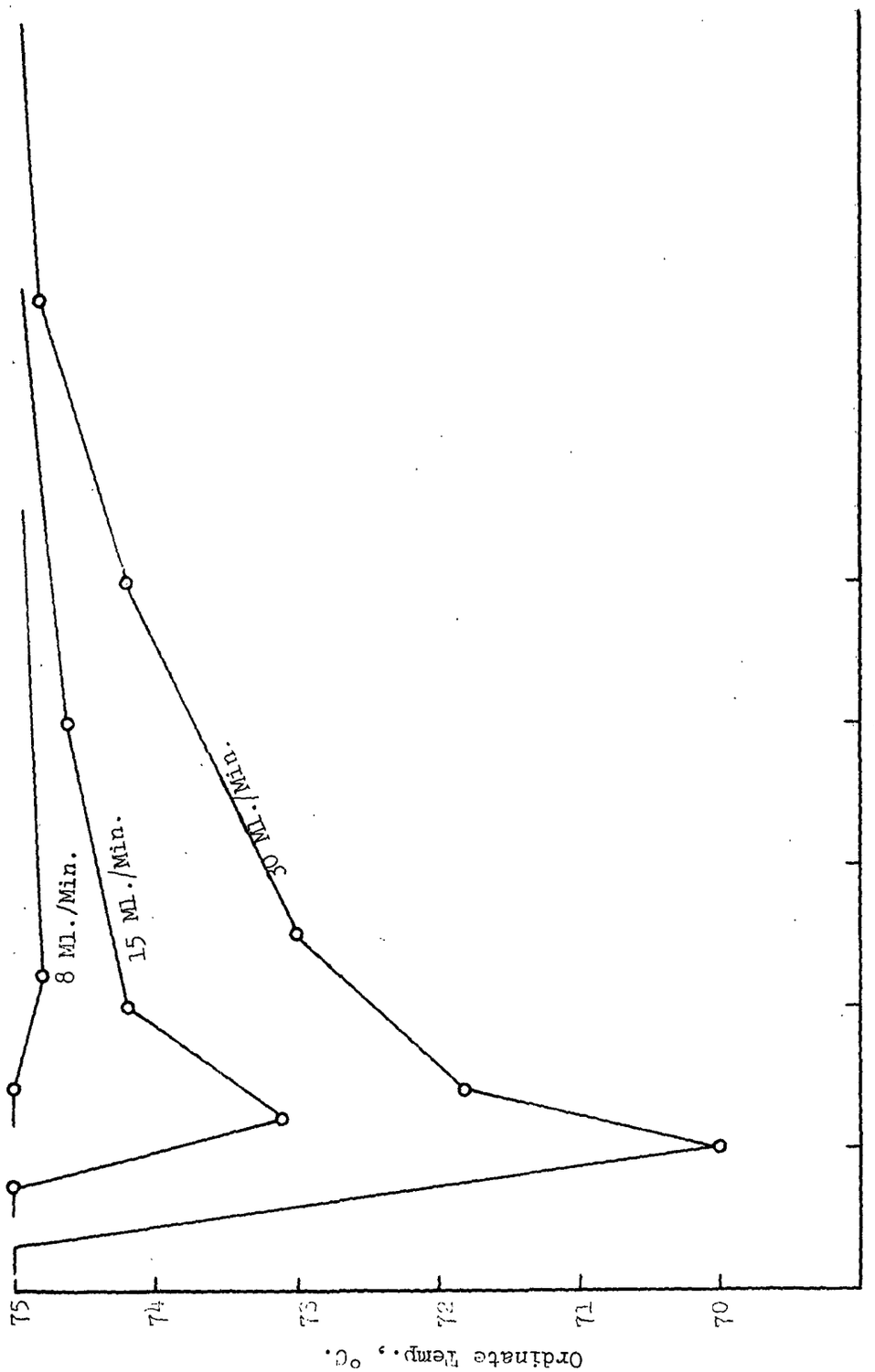


Figure 22. Temperature Equilibration at 75°C.

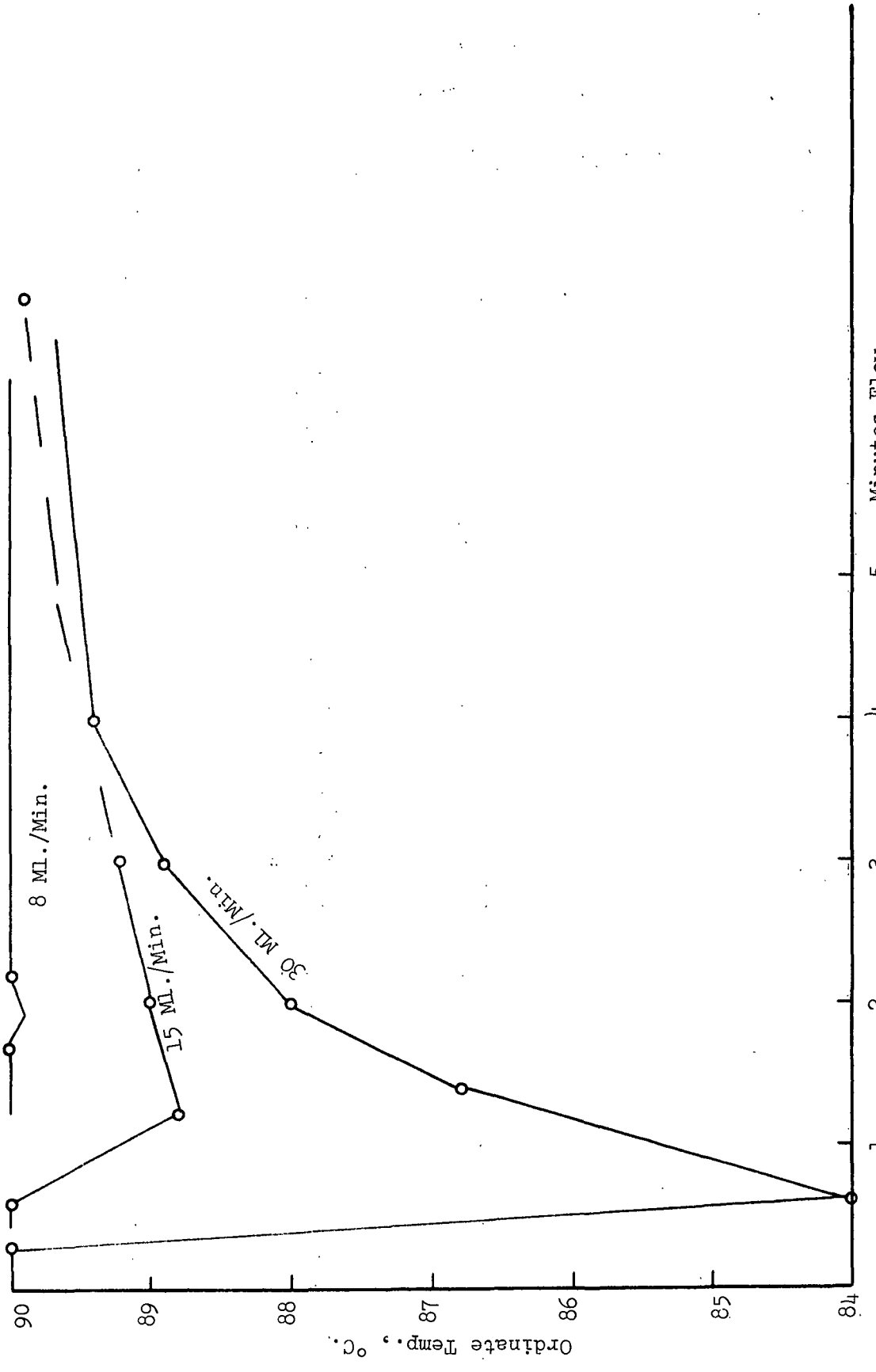


Figure 23. Temperature Equilibration at 90°C.

TABLE XIII

TEMPERATURE CHANGES AT VARIOUS FLOW RATES

Bath Temperature, °C.	Flow Rate, ml./min.	Time, min.	Potentiometer, millivolts	Temperature, °C.
60	30	0	0.095	60
		0.6	0.35	55.4
		1.5	0.23	57.4
		2	0.20	58.1
		4	0.15	58.7
		10	0.13	59.4
60	15	0	0.125	60
		0.5	0.125	60
		0.7	Deflection	
		1.4	0.23	58.1
		2	0.18	58.9
		6	0.14	59.6
60	8	0	0.14	60
		0.5	0.14	60
		1.5	Deflection	
		2.6	0.16	59.6
		10	0.155	59.7
60	4	0	0.155	60
		4.6	0.160	60
		6	0.160	60
		14	0.160	60
75	30	0	0.16	75
		0.3	Deflection	
		1.0	0.45	70
		1.4	0.33	71.8
		2.5	0.27	73
		5	0.20	74.2
		7	0.17	74.8
75	15	0	0.16	
		0.7	Deflection	
		1.2	0.26	73.1
		2	0.20	74.2
		4	0.19	74.6
75	8	0	0.14	75
		1.4	Deflection	
		2.2	0.15	74.8
		3.5	0.14	75
90	30	0	0.13	90
		0.3	Deflection	
		0.6	0.50	83.4
		1.4	0.30	86.6
		2	0.24	88.0
		4	0.16	89.4
90	15	0	0.115	90
		0.6	Deflection	
		1.2	0.22	88.0
		2	0.16	89.0
		3	0.15	89.2
		7	0.12	89.9
		11	0.115	90
90	8	0	0.115	90
		1.7	Deflection	
		2.2	0.12	90
		3	0.12	90

less "square" curve at its latter stage. They speak of vortices and turbulent eddies producing convective mixing in the direction of flow. Also, the velocity of distribution of flow is not uniform (parabolic front); this is typical of laminar flow. Molecular diffusion is a minor factor.

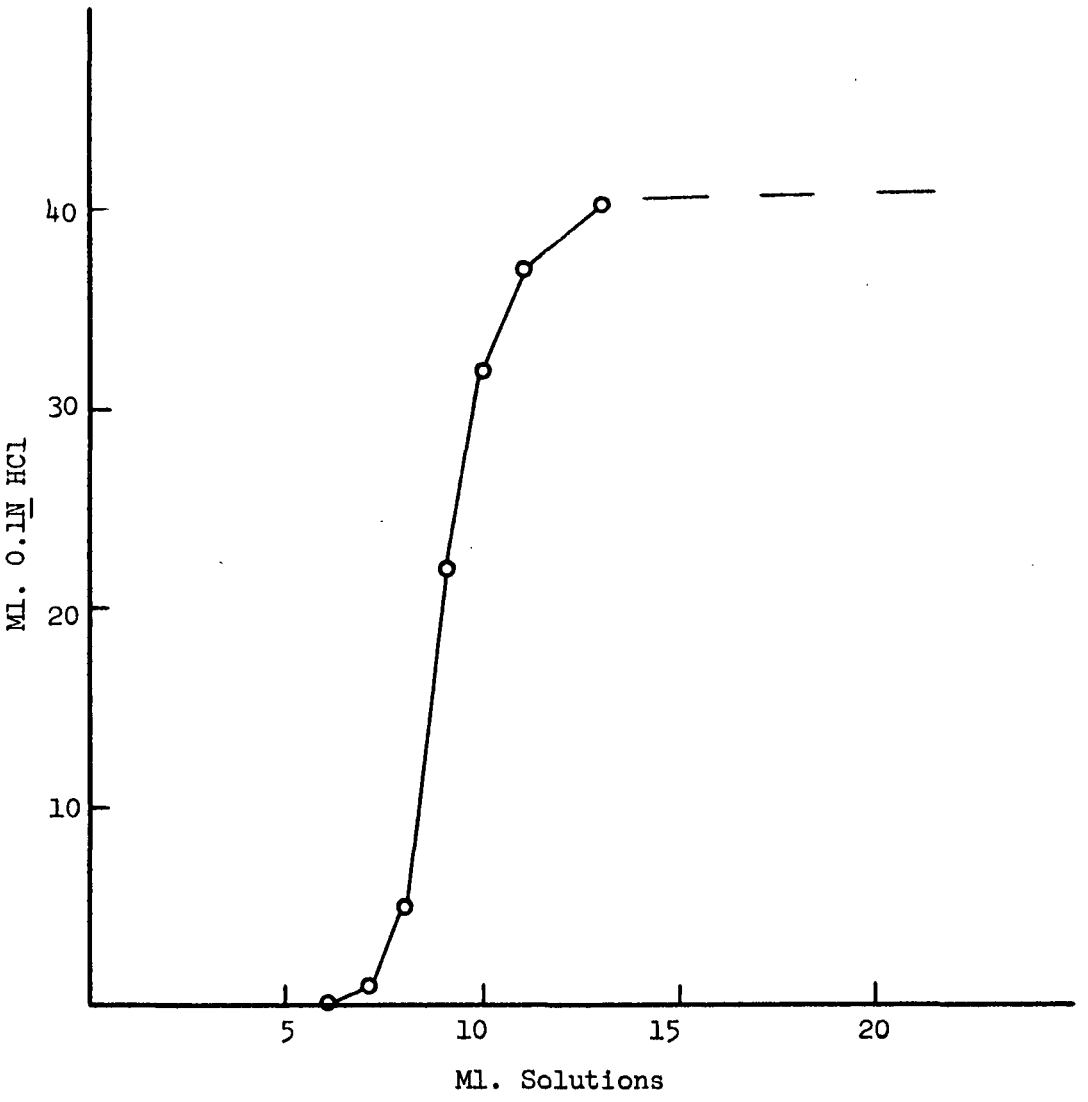


Figure 24. Plug Flow in a Heating Coil

The experimental data for Fig. 24 were obtained by filling a 8-foot 1/8-inch O.D. tube (0.089-inch I.D.) with water, and then displacing this with 2N sodium hydroxide. The flow rate was 4 ml./min. and samples were taken at 15 and 30-second intervals and titrated with 0.1N hydrochloric acid. Experiments run intermittently or continuously gave the same results; there was no back-wash or surge when the flow was stopped, and then started again.

PRESSURIZED FLOW REACTOR

DESCRIPTION OF TOTAL ASSEMBLY

A pressurized flow reactor is under construction; it consists of a pressurized chamber containing three syringes and two driving motors. The heating and reaction coils emerge from the chamber into the oil bath and then return to the chamber again. This closed loop system is shown in Fig. 25; it provides the same pressure at the syringe and quenching end of the system. So no pressure packings are required for the syringes and there is no problem of the quenched sample coming out of the open end of a pressurized system.

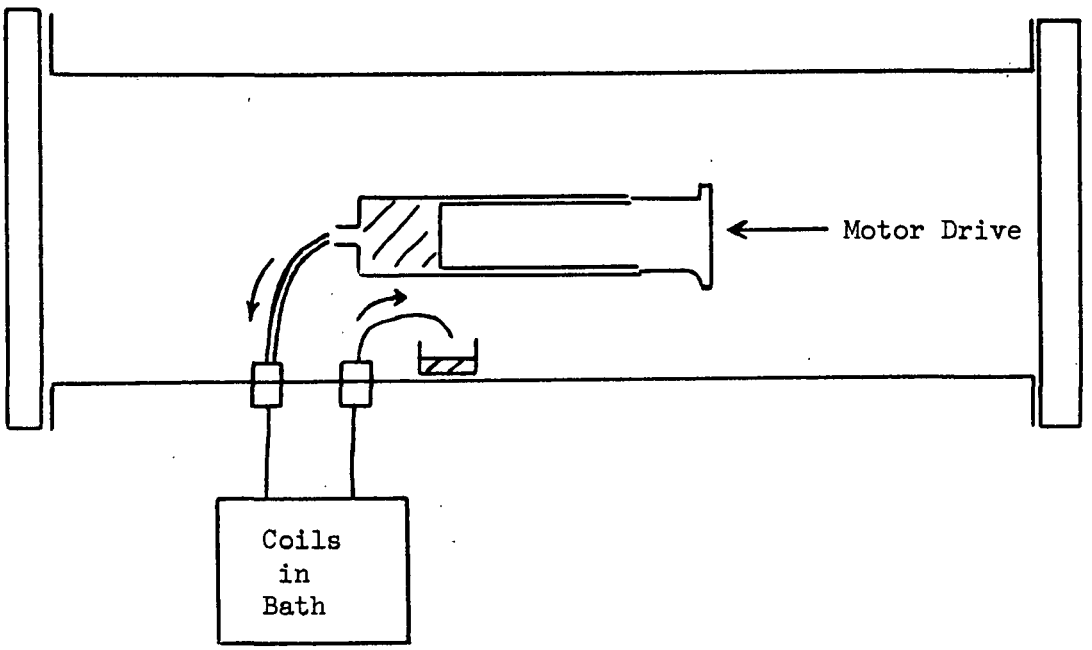


Figure 25. Pressurized System with Closed Loop

The pressure chamber is a piece of flanged pipe, 8 inches inside diameter and 52 inches in length; the wall thickness is 0.375 inch. The three syringes will be placed, with the driving motors, inside. The electrical controls will be outside. The syringes will be connected by bulkhead fittings to a series of valves leading to the heating and reaction coils. A sketch of these details is shown in Fig. 26.

The interior of the chamber, about 1-cubic foot volume, will be filled with nitrogen to the appropriate pressure (up to 150 pounds) to prevent boiling of liquids in the heating and reaction coils.

Operation of such a reactor will be "blind" in that the motion of the syringes cannot be seen, but this disadvantage will be offset by the absence of pressure-resistant syringes and packings, and there will be no problem of having either an open end to the atmosphere (a capillary to maintain pressure) or a "floating piston" type of receiving chamber at the end of the flow system.

The valves (Off-On Whitey Ball valves) and the Swagelok fittings for connecting the several components are of stainless steel and capable of operating under pressure and with concentrated alkali. The valves and syringes will be operated at room temperature; only the heating and reaction coils and one mixer will be operated by the higher reaction temperatures. Both of the mixers are of the Gibson eight-jet mixer types and are being constructed of stainless steel.

The pressure chamber has already been constructed and ready for use. The valves and mixers have been ordered and should be available shortly. A cradle will be constructed to hold the pressure chamber (weight about 300 lbs.)

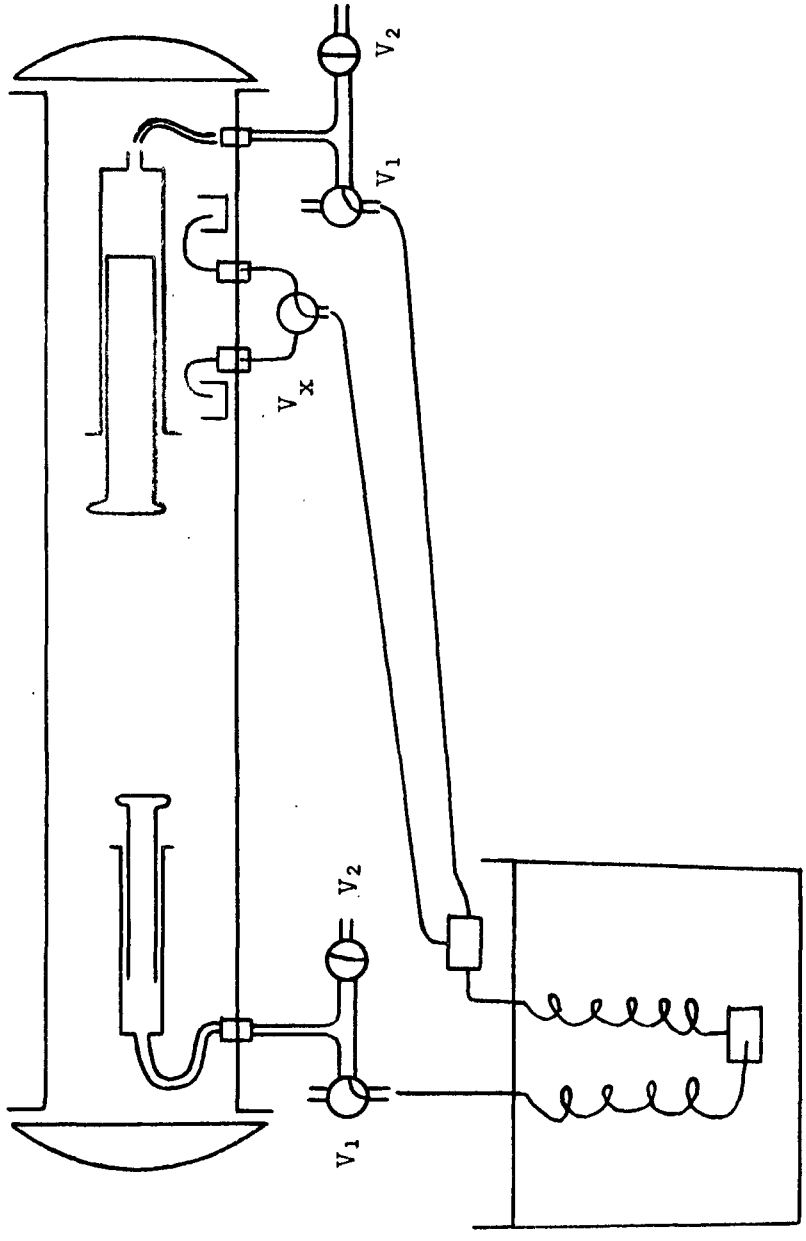


Figure 26. Pressurized Flow Reactor (Only One 20-Ml. Syringe is Shown)

so that the system of coils can be lowered into and raised from the oil bath, in a manner similar to the action of the Lab-Jack for the flow reactor operating at atmospheric pressure.

With the present syringe pumps and short reaction coils a reaction time of about 1.5 sec. can be handled in this reactor. The time can be shortened by use of faster driving motors, but a minimum time of about 0.1 sec. is caused by the limitations of mixing (10). With shorter times, mixing becomes an appreciable error in the total dwell time in the reaction coil (see Fig. 17). Also, the time of chemical reaction of boric acid with the alkali (quenching) is a negative factor. However, as a compensation, the rapid reduction in temperature by mixing 5 volumes of cold boric acid with 1 volume of hot alkaline solution is a positive factor in slowing the alkaline reaction rapidly.

PROPOSED OPERATION

The several syringes will be filled manually, with a 1/8-inch O.D. stainless tubing, connected by a short piece of rubber tubing. This tubing will be partly filled with liquid also. The syringe will be inverted temporarily to remove air bubbles.

Each syringe will then be mounted on the holder base within the pressure chamber and the Swagelok fitting fastened to the inner end of the bulkhead fitting. The syringe pump is started and liquid pumped through the bulkhead fitting to fill the tee between V_1 and V_2. For the F_1 arrangement Fig. 27, is used. When liquid emerges from both valves, V_2 is closed (F_2 arrangement). Now we have solution from the filled syringe to the bore in valve V_1.

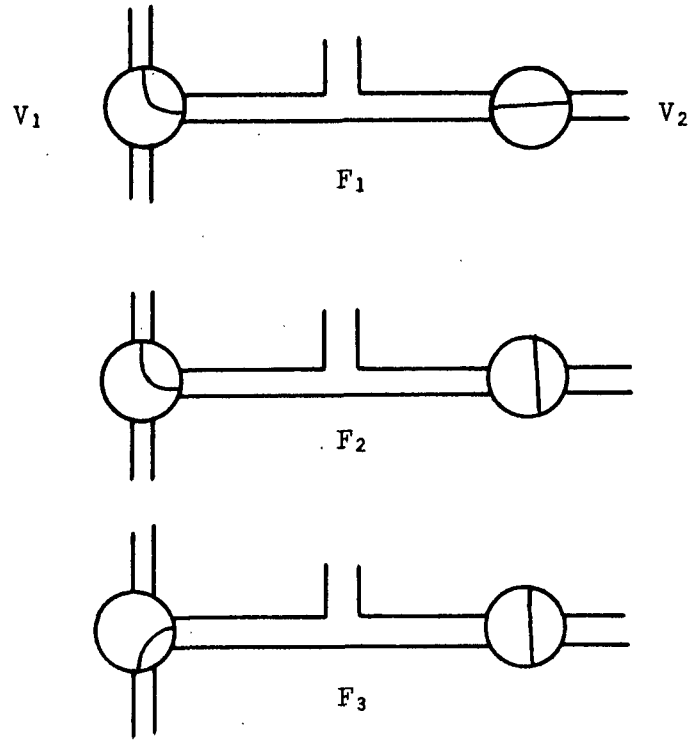


Figure 27. Valve Arrangement for Pressurized Reactor

Valve V_1 has a Swagelok fitting on the lower arm, and the appropriate heating coil or feeder tube (in the case of the boric acid syringe) is attached at this point. The bore of the valve provides a sharp dividing line between the solution and the empty tubing.

All three syringes are connected in this manner, and the quench line from the second mixer connected by two bulkhead fittings to lead into the pressure chamber again. Valve V_1 is then turned to F_3 arrangement, the chamber capped, and pressurized. In this arrangement the liquid in the syringes will be "open" at both ends, at the syringe plunger and at valve V_1, leading through the system

of coils and mixers and valve V_x to the container again. Thus, there will be no pressure differential in the system.

After the desired pressure is obtained, the syringe pumps are started, as for the system with the previous flow reactor. Operation may have to be intermittent: (a) sugar solutions and alkali pumped into the heating coils and flow stopped to allow temperature equilibration, (b) flow started again to provide mixing, and (c) boric acid added at the appropriate time to provide quenching.

The adjustment on valve V_x will be such that the quenched solution will be fed into the beaker at Q. The pumps will then be stopped, and valve V_x charged to feed into the waste beaker W. Then the system will be slowly depressured, and any liquid forced from the coil system by released gases will be spilled into W.

The above system is set up with the bulkhead fittings mounted in the body of the pressure chamber; the end plates are put on at the last minute after adjustment of liquid leading to valve V_1. The bases holding the driving motors and syringes within the chamber can be readily moved, and will be held only by the tubing leading to the bulkhead fitting.

An alternate system would be to run all bulkhead fittings through the end plates and mount the motor base, syringes, and end plate on a runway so that the whole assembly can be readily moved in and out as a unit. Special bulkhead fittings will be needed for this, as the end plates are one-inch thick and the available fittings are designed for 1/2-inch bulkheads. We are limited by safety factors at present to the one-inch thickness for the flat end plates whereas a 3/8-inch wall thickness can be used for the pipe wall.

FUTURE WORK

Future efforts will be concentrated on getting the pressurized reaction into operation as rapidly as possible, so that kinetic runs can be made at higher temperatures. While this assembly is going on, kinetic runs will be made at 75 and at 90° with the unpressurized reactor, to check the extrapolated rates mentioned in this report.

The reaction times for the kinetic runs at 75 and 90° can be handled by the present flow reactor. However, for higher temperatures and faster reactions, the possibility of using driving motors with greater speeds will be explored. The speed of the present motors, 30 to 100 ml./min., is relatively slow, and a faster driving speed should be possible.

The immediate problem to solve is the rate of the peeling reaction at higher temperatures, preferably under the conditions of kraft pulping. Then, once a base line is established, the variables, such as alkali concentration, ionic strength, buffer solutions, sulfidity, can be explored. If the proposed base line, 2N sodium hydroxide at 150°, is too fast to study, then a new base line will have to be established.

The various cooperators will have thoughts about the direction of research on this project also.

ACKNOWLEDGMENTS

Acknowledgment for assistance in this work are made to certain members of the Institute Staff: to Fred Haigh for the gas chromatographic analysis and calibration of the thermocouple, to Keith Hardacker for electrical circuits, and to Marvin Filz and Paul Van Rossum for machine work. Also we are grateful to N. Chang, R. A. Holm, R. Larsen, L. Dambruch, and M. Godschalx for assistance in design of equipment.

LITERATURE CITED

1. Progress Report One, Project 2942, Dec. 18, 1970, p. 4.

2. Lindberg, B., Theander, O., and Uddegard, J. E., Svensk Papperstid. 69:360 (1966).

3. MacLaurin, D. J., and Green, J. W., Can. J. Chem. 47:3947, 3957(1969).

4. Best, E. V., and Green, J. W., Tappi 52:1321(1969).

5. Progress Report One, Project 2942, Dec. 18, 1970, p. 10.

6. Schroeder, L. R., and Green, J. W., J. Chem. Soc. 1966:530-1.

7. Pinsent, B. R. W., Discn. Faraday Soc. 17:140(1954); Miettine, J. K. In Chance, Gibson, Eisenhardt, and Longberg-Holm's Rapid mixing and sampling techniques in biochemistry. p. 306. New York, Academic Press, 1964.

8. Gibson, Q. H., and Milnes, L., Biochem. J. 91:161(1964).

9. Kramers, J., and Westerterp, K. R. Elements of chemical reactor design and operation. p. 70. New York, Academic Press, 1963.

10. Caldin, E. F. Fast reactions in solution. p. 9. New York, John Wiley, 1964.

THE INSTITUTE OF PAPER CHEMISTRY

Leland R. Schroeder
Research Associate

John W. Green
Senior Research Associate
Division of Natural
Materials & Systems